air

Dry Deposition Monitoring Methods in Alberta

Alberta
Environment

Dry Deposition Monitoring Methods in Alberta

Prepared for:
Alberta Environment
Edmonton, Alberta

Final Report

By:
WBK & Associates Inc.
St Albert, Alberta

March 2006

ISBN: 978-0-7785-7583-2 (Printed)
ISBN: 978-0-7785-7584-9 (On-line)
Web Site: http://www.gov.ab.ca/env/

Any comments, questions, or suggestions regarding the content of this document may be directed to:

Air Policy Branch
Alberta Environment
11th Floor, Baker Centre
10025-106 Street
Edmonton, AB
T5J 1G4
Fax: (780) 644- 8946

Additional copies of this document may be obtained by contacting:

Information Centre
Alberta Environment
Main Floor, Oxbridge Place
9820 – 106th Street
Edmonton, Alberta T5K 2J6
Phone: (780) 427-2700
Fax: (780) 422-4086
Email: env.infocent@gov.ab.ca

FOREWORD

Acid deposition occurs when acidifying pollutants emitted from anthropogenic and other processes undergo chemical reactions in the atmosphere and fall to the earth as wet deposition (rain, snow, cloud, fog) or dry deposition (dry particles, gas). Acidic pollutants can be transported long distances in the atmosphere from their sources and eventually be deposited in ecosystems over broad regional scales and in locations far from the emission sources.

Dry deposition is generally more a local problem than wet deposition. Direct measurement of dry deposition rates is difficult. Dry deposition depends on many factors, including: meteorological conditions, characteristics of the pollutants being deposited (e.g. different gaseous chemical and particle size), and characteristics of the surface on which deposition occurs.

The most accepted and common method for estimating dry deposition is the so-called "inference method." The inferential method is a combination of measurement and modeling that involves indirect estimation of dry deposition rates on the basis of routinely measured air concentrations and meteorological parameters. The method is based on an assumed steady-state relationship $F = V_d C$, where the dry deposition flux or rate (F) is a product of the dry deposition velocity (V_d) and the concentration (C) of an airborne pollutant.

A series of studies have been initiated by AENV to evaluate the inference method and search for the most suitable and simple model for deposition rate estimations in Alberta. This report documents the second study in the series. Titles for the reports of the other studies are: *"Review and Assessment of Methods for Monitoring and Estimating Dry Deposition in Alberta"*, and *"Refinement Study of Dry Deposition Inference Method Used in Alberta"*. It is anticipated that once all necessary information is gathered, an Alberta protocol for dry deposition measurement will be prepared.

Lawrence Cheng, Ph. D.
Air Policy,
Climate Change, Air and Land Policy Branch

SUMMARY

Currently there is no standard method for field measurement and estimation of dry deposition of acidifying pollutants in Alberta. Alberta Environment is pursuing development of an inexpensive standard method. This may involve a combination of continuous, intermittent, and/or passive field measurements of acidifying pollutants and using inference methods for estimating sulphur and nitrogen species dry deposition. An overall objective of this study was to continue evaluating inferential methods for estimating dry deposition rates.

Dry Deposition Methods Evaluation

Three different inference methods used in Canada were evaluated for estimating sulphur and nitrogen species dry deposition. These methods were developed by Alberta Environment (AENV), Environment Canada (ENVC), and the Wood Buffalo Environmental Association (WBEA). A specific objective was to use these inference methods to compare contributions of gaseous SO_2, NO_2, HNO_3, HNO_2, and particulate forms of sulphur (SO_4^{2-}) and nitrogen (NO_3^- and NH_4^+) in total sulphur and nitrogen deposition and their potential relationships among each method. Another specific objective was to identify and recommend a preferred method (or methods) that could be routinely used for estimating sulphur and nitrogen species dry deposition rates. The following findings are noted:

1. Complete sulphur and nitrogen gaseous and particulate species and meteorological data for a one-year period (2003) from the Wood Buffalo Environmental Association Fort McKay air monitoring station were evaluated using the three methods. All three methods showed a similar ability to represent variation in dry deposition rates for individual species from month to month.

2. The WBEA method yielded higher monthly deposition rates for most species modeled (SO_4^{2-}, NO_2, HNO_3, HNO_2, and NH_4^+) compared to the AENV and ENVC methods. Monthly potential acid input (PAI) associated with dry species for each method is shown in Figure ES-1. The WBEA method also yielded higher PAI associated with dry species compared to the AENV and ENVC methods during winter and spring. The WBEA method gave similar PAI values associated with dry species during summer and fall. A simpler computational approach for aerodynamic and surface resistance terms in the WBEA method may partially explain differences observed during winter and spring. Further testing would be required to better understand whether this is the case.

3. Annual total PAI associated with dry species for 2003 was 0.14 kg H^+/ha/yr (AENV method), 0.15 kg H^+/ha/yr (ENVC method), and 0.20 kg H^+/ha/yr (WBEA method). The higher annual rate observed for the WBEA method relative to other methods is consistent with higher monthly deposition rates for individual species. While the AENV and ENVC methods yielded comparable monthly PAI values associated with dry species, it is observed that ENVC input

parameters have more boundary conditions (i.e. cut-off points and lower/upper limits) associated with their use compared to AENV input parameters.

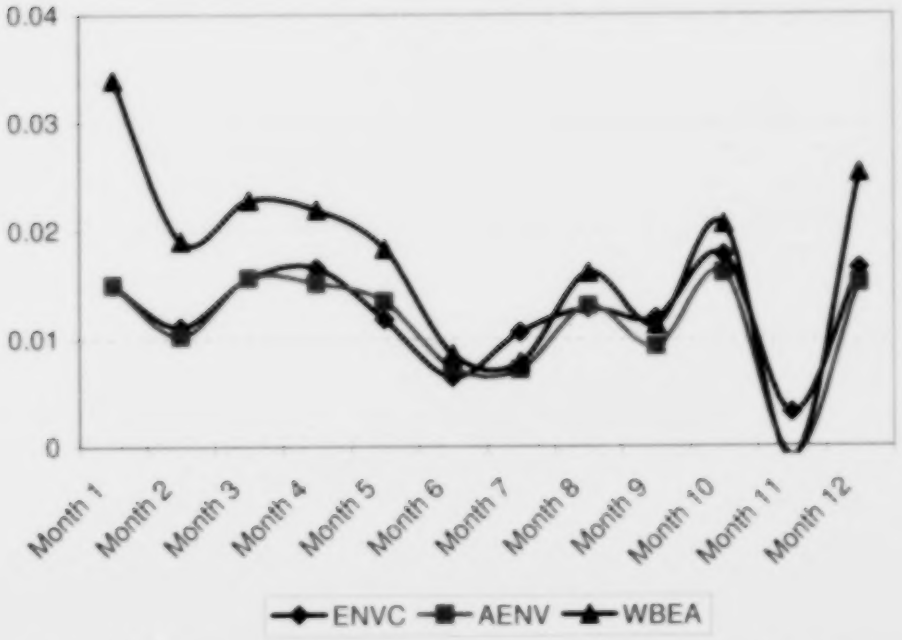


Figure ES-1. Monthly potential acid input (PAI) values associated with dry species for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg H+/ha/month).

(ENVC = Environment Canada method; AENV = Alberta Environment method; WBEA = Wood Buffalo Environmental Association method)

4. The ENVC method is more complicated given that it has the greatest number of input parameter requirements. A number of additional assumptions for some of the input parameters are also required before modeling can be performed. The AENV method provided comparative results to the ENVC method. The AENV method is less complicated compared to the ENVC method, and it requires less input data and computing time. The WBEA method is simple and straight-forward to use. However, this method yielded higher monthly deposition rates for most species modeled compared to the other methods using the 2003 dataset.

5. The dataset used to evaluate the methods was short – one year – and month to month variation or lack of variation in species deposition rates observed using each method does not necessarily provide an indication of what may happen in other years. Although only a one-year dataset was available for evaluation,

results support that the AENV method offers a practical choice for routine computation of sulphur and nitrogen species dry deposition in Alberta. Further testing using different datasets elsewhere in Alberta is recommended to support this. If the ENVC method can be shown to provide comparable results to the AENV method using different datasets, it would offer a logical choice for periodic use as a check on the AENV method.

6. Evaluation of contributions of SO_2 and NO_2 deposition in total sulphur and nitrogen species deposition at the Fort McKay site indicated that about 82% is in the form of gaseous SO_2 with the remainder as particulate SO_4^{2-} (18%). These results are comparable to annual deposition loadings of sulphur species during 1998 to 2002 at the former Alberta Environment Beaverlodge acid deposition monitoring site (80% in the form of gaseous SO_2 and 20% as particulate SO_4^{2-}).

   Estimates of annual nitrogen species deposition at the Fort McKay site indicated that ~51% was from NO_2 with the remainder as HNO_3 and HNO_2 (35%) and particulate NH_4^+ and NO_3^- (<14%). Estimates of annual nitrogen species deposition at the Beaverlodge site during 1998 to 2002 showed that about 35 to 50% was from NO and NO_2 with the remainder as HNO_3 and HNO_2 (40 to 60%) and particulate NH_4^+ and NO_3^- (<10%).

7. Future work evaluating these inference methods should consider the influence of assigning additional boundary conditions to AENV model input parameters on variability associated with model outputs. Specifically, assigning boundary conditions to AENV input parameters consistent with default ENVC model assumptions should be investigated to better understand whether these changes have the ability to improve AENV model performance relative to the ENVC model.

TABLE OF CONTENTS

FOREWORD i
SUMMARY ii
LIST OF TABLES vi
LIST OF FIGURES vii

1.0 INTRODUCTION 1
1.1 Objectives of Study 1

2.0 DRY DEPOSITION METHODS EVALUATION 3
2.1 Background on Inference Method 3
2.2 Methods Description 6
2.2.1 Alberta Environment Method 6
2.2.2 Environment Canada Method 6
2.2.3 Wood Buffalo Environmental Association Method 7
2.3 Methods Assumptions 8
2.4 Results and Discussion 13
2.4.1 Model Results 13
2.4.2 Comparison of Inference Methods 22
2.4.3 Relationships of Dry Deposition for Sulphur and Nitrogen Species 24
2.4.3.1 Ratio 24
2.4.3.2 Ratio 25
2.4.3.3 Ratio 26
2.4.3.4 Ratio 26

3.0 FINDINGS AND RECOMMENDATIONS 27

4.0 REFERENCES 29

Appendix I 33

Appendix II 40

Appendix III 58

LIST OF TABLES

Table 1. Species commonly measured for dry deposition using the inference method..... 5

Table 2. Dry deposition model parameters for Wood Buffalo Environmental Association Fort McKay air monitoring station – AMS #1 – for the period 1 January 2003 to 31 December 2003. 8

Table 3. Relative comparison of selective features of three inference methods for estimating dry deposition..... 23

Table 4 Ratio of annual SO_2 deposition to total sulphur species deposition at WBEA Fort McKay air monitoring station during 2003. 24

Table 5 Ratio of annual NO_2 deposition to total nitrogen species deposition at WBEA Fort McKay air monitoring station during 2003. 25

Table 6. Ratio of annual SO_2 deposition to total sulphur species deposition at Beaverlodge, Alberta (after WBK, 2008). 26

Table 7. Ratio of annual NO_x deposition to total nitrogen species deposition at Beaverlodge, Alberta (after WBK, 2008). 26

LIST OF FIGURES

Figure ES-1 Monthly potential acid input (PAI) values associated with dry species for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1. iii

Figure 1. Relative locations where dry deposition resistance factors R_a, R_b, and R_c apply. 4

Figure 2. Location of acid deposition monitoring site (Fort McKay, AMS #1) among oil sand lease holders in Wood Buffalo Environmental Association zone (after COST, 2006). 10

Figure 3. Monthly sulphur dioxide (SO_2) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg SO_2/ha/month) 14

Figure 4. Monthly sulphate (SO_4^{2-}) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg SO_4^{2-} /ha/month). 15

Figure 5. Monthly nitrogen dioxide (NO_2) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg NO_2/ha/month). 16

Figure 6. Monthly nitric acid (HNO_3) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg HNO_3/ha/month) 17

Figure 7. Monthly nitrous acid (HNO_2) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg HNO_2/ha/month) 18

Figure 8. Monthly nitrate (NO_3^-) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg NO_3^- /ha/month) 19

Figure 9. Monthly ammonium (NH_4^+) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg NH_4^+/ha/month). 20

Figure 10. Monthly potential acid input (PAI) values associated with dry species for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg H^+/ha/month). 21

1.0 INTRODUCTION

Acid deposition occurs when acidifying pollutants emitted from anthropogenic and other processes undergo complex chemical reactions in the atmosphere and fall to the earth as wet deposition (rain, snow, cloud, fog) or dry deposition (dry particles, gas). The main chemical precursors leading to acidic pollutants are sulphur dioxide (SO_2) and oxides of nitrogen (NO_x). Reactions of these pollutants with water, oxygen, carbon dioxide, and sunlight in the atmosphere produce acidic pollutants, e.g. sulphuric acid (H_2SO_4), nitric acid (HNO_3), and nitrous acid (HNO_2). These and other acidic pollutants can be transported long distances in the atmosphere from their sources and eventually be deposited in ecosystems over broad regional scales and in locations far from the emission sources.

Dry deposition refers to removal of aerosol pollutants through eddy diffusion and impaction, large particles through gravitational settling, and gaseous pollutants through direct transfer from air to water via gas exchange. Dry deposition involves acidic sulphur and nitrogen pollutants (gases or particles) from the atmosphere being retained by the earth's surface. At the same time, co-deposition of base cations (e.g. Na^+, Mg^{2+}, Ca^{2+} and K^+) results in a reduction of the amount of deposited acidity.

Potential acid input (PAI) provides a method of representing total acidic deposition (Cheng et al., 2001). PAI includes both wet and dry deposition. PAI is calculated by subtracting neutralizing capacity (base cation deposition) from deposition of acidic substances (e.g. sulphur and nitrogen species). Cheng et al. (2001, 1997) provide a detailed description of the estimation of total PAI. The PAI method does not include processes that remove acidity from the earth's surface (leaching, runoff, etc.).

1.1 Objectives of Study

Currently there is no standard method for the field measurement and estimation of dry deposition of acidifying pollutants in Alberta. Alberta Environment is pursuing development of an inexpensive technique for measuring and using inference methods for estimating sulphur and nitrogen species dry deposition. WBK (2008) reviewed current approaches used for measuring and estimating dry deposition.

An overall objective of this current study was to continue evaluating inferential methods for estimating dry deposition after WBK (2008). The purpose was to further investigate inferential methods that can be used by government and industry in Alberta for improved acid deposition management. Three different inference methods used in Canada for estimating sulphur and nitrogen species dry deposition were evaluated. A specific objective was to compare contributions of gaseous SO_2, NO_2, HNO_3, HNO_2, and particulate forms of sulphur and nitrogen in total sulphur and nitrogen dry deposition and identify potential relationships of each method. Another specific objective was to

identify and recommend a preferred inference method (or methods) that could be routinely used for estimating sulphur and nitrogen species dry deposition rates in Alberta.

2.0 DRY DEPOSITION METHODS EVALUATION

The Wood Buffalo Environmental Association (WBEA) collected complete sulphur and nitrogen gaseous and particulate species and meteorological data at the Fort McKay air monitoring station – AMS #1 – during 2003. These data were used to evaluate relationships of sulphur and nitrogen species deposition using three inference methods applied in Canada. These methods were developed by:

- Alberta Environment (Cheng et al., 2001).
- Environment Canada (Zhang et al., 2003a, 2003b, 2002a, 2002b, 2001a, and 2001b).
- WBEA Terrestrial Environmental Effects Monitoring (TEEM) Committee (EPCM, 2002, 2000).

A specific objective of the evaluation was to compare contributions of gaseous SO_2, NO_2, HNO_3, HNO_2, and particulate forms of sulphur (SO_4^{2-}) and nitrogen (NO_3^- and NH_4^+) in total sulphur and nitrogen deposition and their potential relationships among each method. Another specific objective of the evaluation was to identify and recommend a preferred inference method (or methods) that could be routinely used for estimating sulphur and nitrogen species dry deposition in Alberta.

2.1 Background on Inference Method

Dry deposition is generally far more a local problem than wet deposition. Estimating dry deposition rates is more difficult. Dry deposition depends on many factors, including: meteorological conditions, characteristics of the pollutants being deposited (e.g. particle size), and characteristics of the surface on which deposition occurs (US EPA, 2001).

A common approach to indirectly estimate dry deposition rates is on the basis of routinely measured air concentrations and meteorological parameters. Continuous and/or integrated measurement techniques are used to record the concentrations of atmospheric pollutants and continuous measurement techniques are used to record meteorological parameters. These parameters are used to estimate dry deposition using the most common method – the inference method (Cheng et al., 2001; Brook et al, 1999a, 1999b; Clarke et al., 1997).

The inference method involves indirect estimation of dry deposition rates on the basis of routinely measured air concentrations and meteorological parameters. The method is based on an assumed steady-state relationship $F = V_d C$, where dry deposition flux or rate (F) is a product of the dry deposition velocity (V_d) and the concentration (C) of an airborne pollutant. V_d is estimated on the basis of resistance models and is defined as the inverse of the sum of multiple resistance factors (aerodynamic resistance (R_a), boundary-layer resistance (R_b), and surface resistance (R_c)) (Wesely and Hicks, 2000, 1977):

$$V_d = \frac{1}{(R_a + R_b + R_c)} \quad (1)$$

Figure 1 illustrates the relative locations where dry deposition resistance factors R_a, R_b, and R_c apply near a surface.

Aerodynamic Resistance (R_a). A shallow sub-layer occurs next to the ground that is within the atmospheric constant flux layer. The depth of this layer is in terms of meters (m) and depends upon atmospheric turbulence and stability, and surface characteristics (Cheng et al., 2001). The atmospheric resistance term, R_a, is used to parameterize the rate of pollutant transfer within this sub-layer as a function of atmospheric turbulence and stability, and surface characteristics (Wesely and Hicks, 1977).

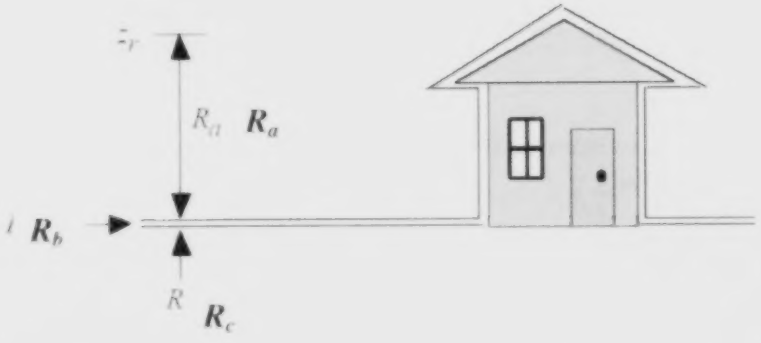


Figure 1. Relative locations where dry deposition resistance factors R_a, R_b, and R_c apply.

Boundary-layer Resistance (R_b). The boundary layer is a thin, non-turbulent layer that develops just above the surface. The depth of this layer is in terms of millimeters (mm). For rough surfaces, this layer is constantly changing and Hicks (1982) reported that is likely to be intermittently turbulent. The rate of pollutant transfer within this layer is determined by molecular diffusion for gases and Brownian diffusion and inertial impaction for particles. The boundary-layer resistance term, R_b, is usually parameterized in terms of the Schmidt number (viscosity of air divided by the diffusivity of the pollutant) and, for particles, the Stokes number (which is a function of the gravitation settling velocity, friction velocity, and the viscosity of air).

Surface Resistance (R_c). Vegetation is a major sink for soluble or reactive gaseous pollutants. After passing through stomata of vegetation, soluble pollutants dissolve in moist mesophyll cells in the interior of leaves (Wesely and Hicks, 1977). Reactive pollutants, e.g. ozone, may also interact with the exterior (cuticle) of the leaves. Due to response of the stomata to external factors such as moisture stress, temperature, and solar

radiation, resistance in the vegetation layer can exhibit significant diurnal and seasonal variability. The surface resistance term, R_c, is usually parameterized in terms of the three main pathways for uptake/reaction of a pollutant within the vegetation or surface (Wesely and Hicks, 1977):

- Transfer through stomatal pores and dissolution or reaction in the mesophyll cells.
- Reaction with or transfer through the leaf cuticle.
- Transfer into the ground/water surface.

Cheng et al. (2001) provide additional information on components that are measured and/or observed in estimating the surface resistance factor.

Atmospheric Pollutants. Atmospheric species commonly measured for dry deposition using the inference method are presented in Table 1. Wesely and Hicks (2000) report that NO dry deposition is usually negligible because of its low solubility and low oxidizing capacity. It is usually not considered for measurement. Cheng et al. (2001) recommend that gaseous ammonia (NH_3) not be considered when estimating dry deposition because sufficient understanding of its biochemistry has yet to be achieved.

Table 1. Species commonly measured for dry deposition using the inference method.

- Sulphur species (gaseous SO_2 and SO_4^{2-} in particulate matter).
- Nitrogen species (gaseous NO_2, acidic gases HNO_3 and HNO_2, and particulate NH_4^+ and NO_3^-).
- Particulate base cations (Na^+, Mg^{2+}, Ca^{2+} and K^+). Co-deposition of these base cations results in a reduction of the amount of deposited acidity.

Particle-associated species derived from erosion of soil or plant material (Na^+, K^+, Mg^{2+}, and Ca^{2+}) tend to reside on larger airborne particles (e.g. >2 µm) (Lovett, 1994). The majority of airborne mass of NH_4^+, SO_4^{2-}, and H^+ reside on submicrometer aerosols. Thus collecting PM_{10} or larger-sized airborne particles (TSP) provide more efficient capture of particle-associated species derived from erosion of soil or plant material.

Concentrations of the eleven species are combined into Equation 2 to estimate potential dry acid input surface load (PAI_{dry}) in kilogram hydrogen equivalents (Cheng et al., 2001):

$$PAI_{dry} = \frac{[SO_2]}{64} + \frac{[NO_2]}{46} + \frac{[HNO_2]}{47} + \frac{[HNO_3]}{63} + 2\frac{[SO_4^{2-}]}{96} + \frac{[NO_3^-]}{62} + \frac{[NH_4^+]}{18} - \left(\frac{[K^+]}{39} + \frac{[Na^+]}{23} + 2\frac{[Ca^{2+}]}{40} + 2\frac{[Mg^{2+}]}{24}\right) \quad [kg\ H^+/ha/yr] \quad (2)$$

Meteorological Parameters. Continuous measurement of numerous meteorological variables is necessary to allow estimation of dry deposition of gaseous and particulate-bound species to specific surfaces using the inference method. Meteorological variables ultimately required are one-hour or 15-minute standard deviation of wind direction, wind speed, solar radiation, and air temperature at standard height (10 m) and near the surface (2 m) (EPCM, 2000). These temperatures are used to establish atmospheric stability. The presence or absence of a wet surface also affects dry deposition. Consequently, surface wetness sensing and relative humidity measurements are required. In summary, continuous measurement of the following meteorological variables is required for estimating gaseous and particulate-bound species dry deposition using the inference method:

- Wind speed and wind speed standard deviation
- Wind direction and wind direction standard deviation
- Solar radiation
- Relative humidity
- Surface wetness
- Air temperature at standard height (10 m)
- Difference in air temperature at standard height and surface (taken as 2 m above ground).

2.2 Methods Description

2.2.1 Alberta Environment Method

Alberta Environment uses an inferential method to estimate aerodynamic (R_a), boundary-layer (R_b), and surface (canopy) resistances (R_c) (Cheng et al., 2001). The method parameterizes dry deposition in terms of a deposition velocity (V_d) that is inferred from measured meteorological parameters and surface characteristics (Equation 1).

Hourly deposition fluxes for each species are calculated as a product of the hourly V_d and the corresponding hourly concentration (C). Total daily dry deposition is the sum of deposition over twenty-four hours. In turn, monthly, seasonal, and annual totals are derived by summing all daily totals for a month, season or year, respectively. WBK (2008) used this method to estimate annual sulphur and nitrogen species deposition using datasets at the Alberta Environment acid deposition monitoring site at Beaverlodge, Alberta for the 1998 to 2002 period. Parameters and equations used in the Alberta Environment method are presented in Appendix I.

2.2.2 Environment Canada Method

Environment Canada uses another variation of the inferential method to estimate dry deposition velocities of acidic species at sites in their national dry deposition monitoring

network (Zhang et al., 2003a, 2003b, 2002a, 2002b, 2001a, and 2001b). Their approach is known as A Unified Regional Air Quality Modeling System (AURAMS) (Zhang et al., 2002a). The network is referred to as the Canadian Air and Precipitation Monitoring Network (CAPMoN) (http://www.msc-smc.ec.gc.ca/capmon/index_e.cfm).

A Big Leaf model is used for gaseous dry deposition in AURAMS (Zhang et al., 2002a). A size-segregated particle dry deposition module originally developed by the Meteorological Service of Canada is used for particle dry deposition in AURAMS (Zhang et al., 2001).

AURAMS was recently revised to include non-stomatal resistance parameterizations (Zhang et al., 2003b). The Big Leaf model developed by Zhang et al. (2002a) was developed for calculating dry deposition velocities for more than 40 gaseous species for AURAMS, but it only included seasonally-adjusted values for non-stomatal resistance. The revised model incorporates non-stomatal resistance parameterizations (Zhang et al., 2003a; Zhang et al., 2002b). Other improvements included more practical treatment of cuticle and ground resistance in winter and handling of seasonally-dependent input parameters.

Similar to the Alberta Environment method, AURAMS uses 1-hour average values of meteorological observations for estimating resistance terms. For a typical 31-day month, 31 x 24 = 744 different hourly meteorological observations are used to compute a similar number of hourly average deposition velocities and deposition loadings for each acidic species. A monthly deposition load is computed by summing individual hourly average loadings (deposition velocity x concentration for each hour). Parameters and equations used in the Environment Canada approach are presented in Appendix II.

2.2.3 Wood Buffalo Environmental Association Method

EPCM (2002, 2000) developed a method for estimating SO_2 and NO_2 dry deposition for the Wood Buffalo Environmental Association Terrestrial Environmental Effects Monitoring (TEEM) Committee. Aerodynamic (R_a) and boundary layer (R_b) resistances are determined using simplified empirical relationships. Surface (canopy) resistance (R_c) is determined using an approach very similar to that used by Alberta Environment. These relationships are described in Appendix III.

The method uses fifteen-minute average values of meteorological observations to estimate resistance terms. For a typical 31-day month, 31 x 24 x 4 = 2,976 different 15-minute meteorological observations are used to compute a similar number of 15-minute average deposition velocities and deposition loadings for each acidic parameter. A monthly deposition load is computed by summing individual 15-minute average loadings for that month.

2.3 Methods Assumptions

WBEA data gaseous and particulate species and meteorological data at the Fort McKay air monitoring station are shown in Table 2. The location of AMS #1 relative to oil sand lease hold areas in WBEA zone is shown in Figure 2. Hourly data for parameters listed in Table 2 were received in electronic form from WBEA. These data were compiled, processed, and evaluated using the three inferential methods mentioned previously.

A number of assumptions were required beyond what each method offered as default assumptions or boundary conditions in order to enable modeling to be performed. These assumptions are listed below. The intent for presenting these assumptions is to allow others to conduct similar model evaluations using the same (or other) inferential methods and dataset.

1. Default characteristics (specific location and land use category) of the Fort McKay air monitoring station (AMS #1):

Latitude	57.2	South Negative
Longitude	-111.6	West Negative
Time zone	-5	West Negative
Reference height (z)	10 m	
Land Use Category (LUC)	Coniferous Forest	

Table 2. Dry deposition model parameters for Wood Buffalo Environmental Association Fort McKay air monitoring station – AMS #1 – for the period 1 January 2003 to 31 December 2003.

Components	Parameters
Combustion gases	Continuous (hourly) SO_2 and NO_2
Acid gases	24-hour integrated annular denuder sample every 6th day for HNO_3, HNO_2, and NH_3
Particulate-associated acidic species	24-hour integrated $PM_{2.5}$ and PM_{10} sample every 6th day for NH^{4+}, SO_4^{2-}, and NO_3^-
Particulate-associated base cation species	24-hour integrated $PM_{2.5}$ and PM_{10} sample every 6th day for Na^+, K^+, Mg^{2+}, and Ca^{2+}
Meteorological parameters (recorded hourly)	Wind speed and wind speed standard deviation Wind direction and wind direction standard deviation Solar radiation Relative humidity Surface wetness Air temperature at standard height (10 m) Difference in air temperature at standard height and surface (taken as 2 m above ground)

2. Data preprocessing procedures:

   a. Invalid or missing hourly data values for were replaced by the month's hourly median value for two or more successive invalid or missing hourly data points.
   b. Invalid or missing hourly data values were replaced by an average of previous and succeeding hourly value for one invalid or missing hourly data point.
   c. Intermittent hourly data (i.e. samples collected for 24 hours every 6th day) were assumed to have the same value for whole 6-day sampling period.
   d. Hourly NO_2 and SO_2 concentrations were converted from ppbv to $\mu g/m^3$ at standard conditions (25 °C and 101.325 kPa).

3. Solar and earth system coordinates:

   Solar zenith angle (θ) and solar radiation (SR) were used in the Environment Canada (WBEA) model and Wood Buffalo Environmental Association (WBEA) model. A Visual Basic program was developed to compute those parameters. The results of this program were confirmed with data obtained from the Astronomical Applications Department, US Naval Observatory (http://aa.usno.navy.mil/).

   In general, if no solar radiation data were available, solar radiation (SR) was assumed equal to 1000*cosine of solar zenith angle (i.e. 1000*cosθ).

4. Alberta Environment model general assumptions:

   Model's equations were adapted from Cheng et al. (2005) and are listed in Appendix I. These equations were programmed in MS EXCEL® using Visual Basic.

   a. Surface resistance (R_c) for all species and boundary-layer resistance (R_b) for particles were weighted based on 54°N latitude for each season.
   b. HNO_3 was assumed to have the same R_b as SO_2.
   c. NH_4^+ was assumed to have the same R_b as SO_4^{2-}.
   d. R_b for NO_3^-, Na^+, K^+, Ca^{2+}, and Mg^{2+} assumed to be the same and half of the R_b of SO_4^{2-}.
   e. R_c for SO_2 and NO_2 were based on default values listed in Table 4.4 and 4.5 of Cheng et al. (2001).
   f. R_c for HNO_3 and HNO_2 was assumed to be equal to 0.1 s/cm for all surfaces and all seasons.
   g. R_c for all particulate species assumed equal to zero.

Figure 2. Location of acid deposition monitoring site (Fort McKay, AMS #1) among oil sand lease holders in Wood Buffalo Environmental Association zone (after COST, 2006).

h. Surface roughness length (z_0) was computed from the wind speed at reference height (u) and standard deviation of the wind direction (σ_θ) when wind speed >6 m/s.

i. No available conditions were available for z_0 for the month of February, 2003. Therefore, the average z_0 of January and March was used to represent conditions for this month.

j. Boundary conditions (cut-off points used) included:
   i. If horizontal wind speed at reference height (u) <0.36 km/h, then $u = 0$ and deposition velocity (V_d) = 0.
   ii. If temperature difference (T_d) = 0, then $V_d = 0$.
   iii. Weighted-average R_c was set constant for each season.

k. Surface wetness conditions:
   i. If precipitation ($Prec$) > 0.1 mm/hour, it is raining and $V_d = V_d$ (wet).
   ii. If relative humidity (RH) >87.4%, it is raining and $V_d = V_d$ (wet).

iii. V_d = Wetness-weighted V_d.

5. Environment Canada model general assumptions:

An electronic file originally programmed using FORTRAN was reprogrammed in MS EXCEL® using Visual Basic. Details of model equations are listed in Appendix II.

Gaseous model component assumptions:

a. Daily precipitation amounts for the Environment Canada Fort McMurray Airport meteorological station were obtained from Environment Canada (Edmonton, AB). The squared hourly cloud fraction was used as an hourly weight to convert daily precipitation to hourly precipitation.
b. Boundary conditions (cut-off points used) included:
   i. If u <3.6 km/h, set $\underline{u}$ = 3.6 km/h.
   ii. If T_d <$1E^{-10}$, set T_d = $1E^{-10}$.
   iii. If Bulk Richardson number (Ri) >0 and solar radiation (SR) >0 w/m^2, set Ri = $1E^{-15}$.
   iv. If Monin-Obukhov Length (L) >5, set L = 5.
   v. If aerodynamic resistance (R_a) <5, set R_a = 5.
   vi. If R_a >1000, set R_a = 1000.
   vii. If R_c <10, set R_c = 10.
c. Surface wetness conditions:
   i. If precipitation ($Prec$) >0.1 mm/h, it is raining.
   ii. If RH >dew point, set RH to dew point.
   iii. If rainy or dew-point condition exist, fraction of stomatal blocking under wet conditions (W_{st}) = (S_{rad} - 200)/800.
   iv. If W_{st} <0.5, set W_{st} = 0.5.
   v. W_{st}-weighted R_c used to calculate V_d.

Particulate model component assumptions:

a. Particulate matter size was assumed to follow lognormal distribution from 0.001 nm to 1 0µm.
b. SO_4^{2-} in particulate form was assumed to follow lognormal distribution with MMD = 0.35 µm and GSD = 2.0.
c. NH_4^+ was assumed to have same V_d as SO_4^{2-}.
d. Na^+ in particulate form was assumed to follow lognormal distribution with MMD = 5.12 µm and GSD = 2.64.
e. NO_3^-, K^+, Ca^{2+}, and Mg^{2+} were assumed to have same V_d as Na^+.
f. Boundary conditions (cut-off points used) included:

i. If u <3.6 km/h, set U = 3.6 km/h.

ii. If T_d <$1E^{-10}$, set $T_d = 1E^{-10}$.

iii. If Ri >0 and SR >0 w/m^2, set $Ri = 1E^{-15}$.

iv. If Monin-Obukhov Length (L) >5, set L = 5.

v. If aerodynamic resistance (R_a) <5, set R_a = 5. p

vi. If R_a >999.9, set R_a = 999.9.

g. No criteria are used for surface wetness conditions.

6. Wood Buffalo Environmental Association (WBEA) model:

Equations for this method were obtained from WBEA Excel files and related documentation (EPCM 2002, 2000) received from the Wood Buffalo Environmental Association. These equations are listed in Appendix III. These equations were programmed in MS EXCEL® using Visual Basic.

This model was developed to process input parameters as 15-minute averages. However model runs used 1-hour average values for input parameter- as 15-minute average values were unavailable.

a. Atmospheric conditions:

a. stable for night time.

b. unstable for day time.

b. HNO_3 assumed to have same R_b as SO_2.

c. NH_4^+ assumed to have same R_b as SO_4^{2-}.

d. R_b for NO_3^-, Na^+, K^+, Ca^{2+}, and Mg^{2+} assumed to be the same and half of R_b of SO_4^{2-}.

e. R_c for SO_2 and NO_2 were based on default values listed in Table 4.4 and 4.5 of Cheng et al. (2001).

f. R_c for HNO_3 and HNO_2 assumed equal to 0.1 s/cm for all surfaces and all seasons.

g. R_c for all particles assumed equal to zero.

h. Boundary conditions (cut-off points used) included:

a. If u <0.36 km/h: set u = 0

b. $R_a \leq 1000$

c. $R_b \leq 1000$

i. Surface wetness conditions:

a. If precipitation (*Prec*) >0.1 mm/hour, it is raining and $V_d = V_d$ (wet).

b. If RH >87.4%, it is raining and $V_d = V_d$ (wet).

2.4 Results and Discussion

2.4.1 Model Results

Individual Species Deposition – Estimated monthly dry deposition rates for a number of sulphur and nitrogen species at the Fort McKay site are presented for each inference method in Figures 3 to 9. Monthly dry deposition rates for sulphur species – SO_2 and SO_4^{2-} – are presented in Figures 3 and 4, respectively. Monthly dry deposition rates for nitrogen species – NO_2, HNO_3, HNO_2, NO_3^-, and NH_4^+ – are presented in Figures 5 to 9, respectively. All deposition rates are expressed in "kg species/ha/month."

As a general observation, all three inference methods show a similar ability to represent changes (variation) in dry deposition rates from month to month. For example, Figure 3 illustrates monthly SO_2 dry deposition rates as kg SO_2/ha/month. The 4th, 7th, and 8th months of the year clearly show higher deposition rates for each method relative to other months. In this particular instance the Environment Canada (ENVC) method yields higher monthly SO_2 deposition rates relative to the other two methods.

Another general observation is made is that the Wood Buffalo Environmental Association (WBEA) method yields higher monthly deposition rates for most species modeled using the 2003 dataset. This includes SO_4^{2-} (Figure 4), NO_2 (Figure 5), HNO_3 (Figure 6), HNO_2 (Figure 7), and NH_4^+ (Figure 9).

Potential Acid Input – Estimated monthly total potential acid input (PAI) associated with dry species at the Fort McKay site are presented for each inference method in Figure 10. These rates are expressed in units of kg H^+/ha/yr and they were computed taking into account all sulphur, nitrogen, and base cation species as shown in Equation 2. Similar to findings reported above, Figure 10 shows that the WBEA method gives higher PAI rates associated with dry species during the winter and spring months using the 2003 dataset.

The WBEA method gives similar rates as the ENVC and AENV methods during other seasons (i.e. summer and fall). It is initially suspected that a simpler computational approach for the aerodynamic (R_a) and surface (R_b) resistance terms in the WBEA method (Appendix III) partially accounts for this departure during winter and spring months. However, further testing would be necessary to better understand whether this is the case.

A general observation is made regarding the performance of each method and their ability to represent change (variation) in monthly total PAI rates associated with dry species shown in Figure 10. The ENVC and AENV method yield comparable monthly total PAI rates associated with dry species, except for the 11th month (November) where the AENV yields a net negative rate. The exact reasons for this departure in the 11th month are unknown, however it may be due to greater equivalent total base cation species deposition flux relative to equivalent total sulphur and nitrogen species flux during the month.

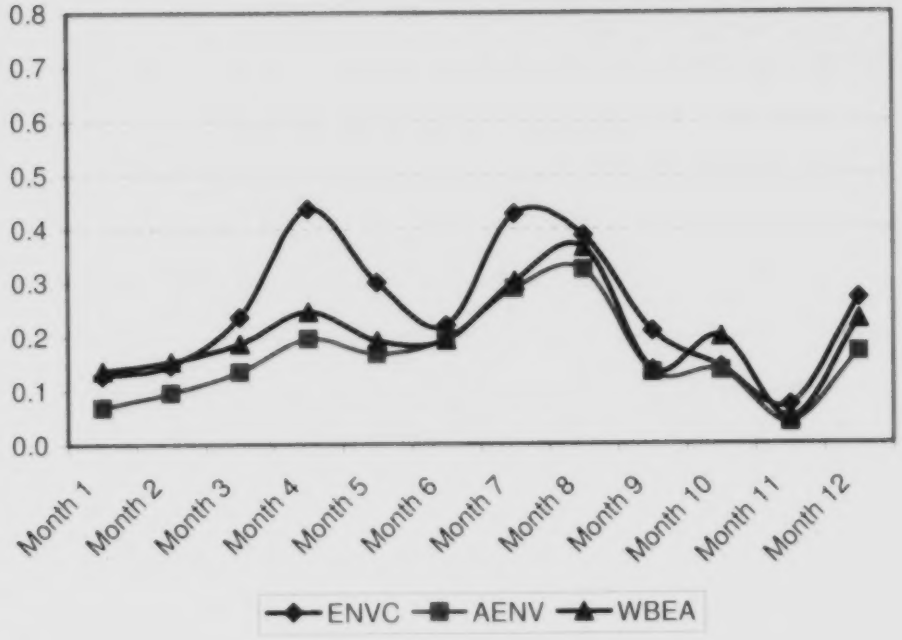


Figure 3. **Monthly sulphur dioxide (SO_2) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg SO_2/ha/month).**

(ENVC = Environment Canada method; AENV = Alberta Environment method; WBEA = Wood Buffalo Environmental Association method)

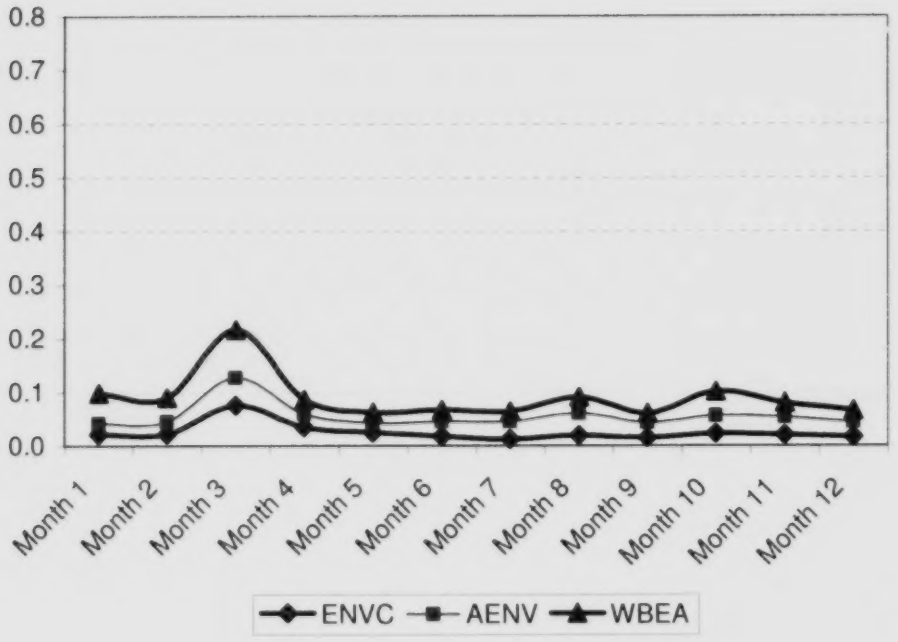


Figure 4. **Monthly sulphate (SO_4^{2-}) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg SO_4^{2-}/ha/month).**

(ENVC = Environment Canada method; AENV = Alberta Environment method; WBEA = Wood Buffalo Environmental Association method)

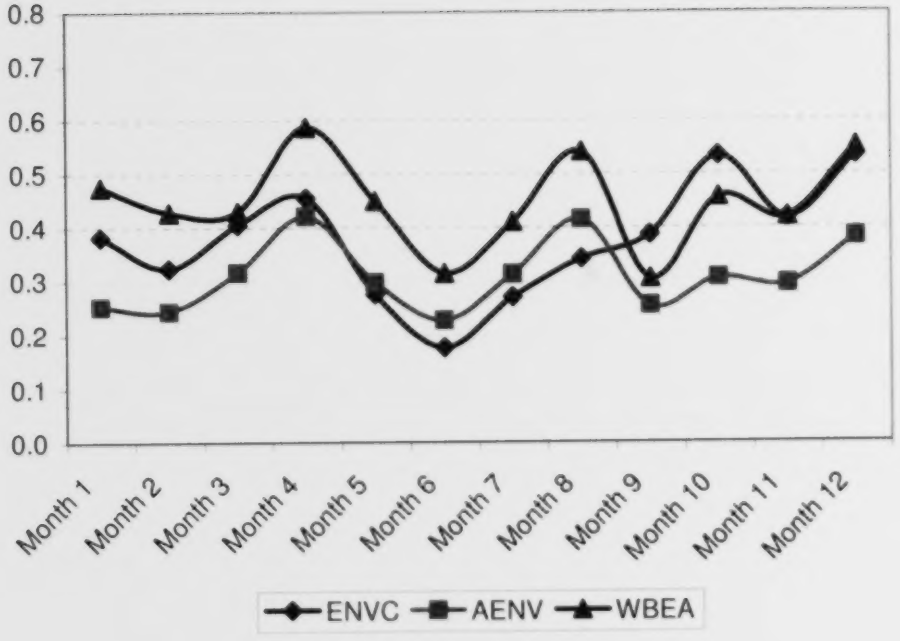


Figure 5. **Monthly nitrogen dioxide (NO_2) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg NO_2/ha/month).**

(ENVC = Environment Canada method; AENV = Alberta Environment method; WBEA = Wood Buffalo Environmental Association method)

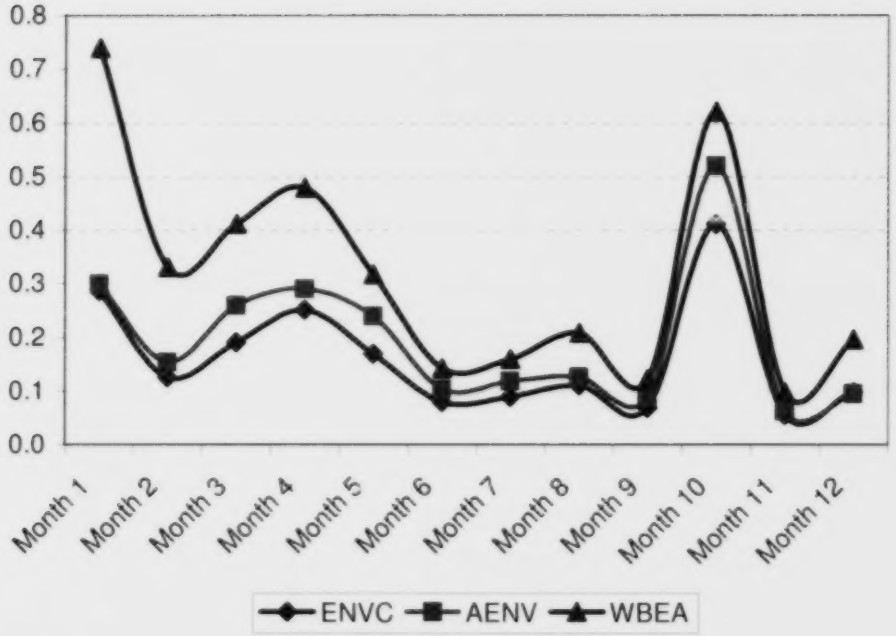


Figure 6. **Monthly nitric acid (HNO_3) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg HNO_3/ha/month).**

(ENVC = Environment Canada method; AENV = Alberta Environment method; WBEA = Wood Buffalo Environmental Association method)

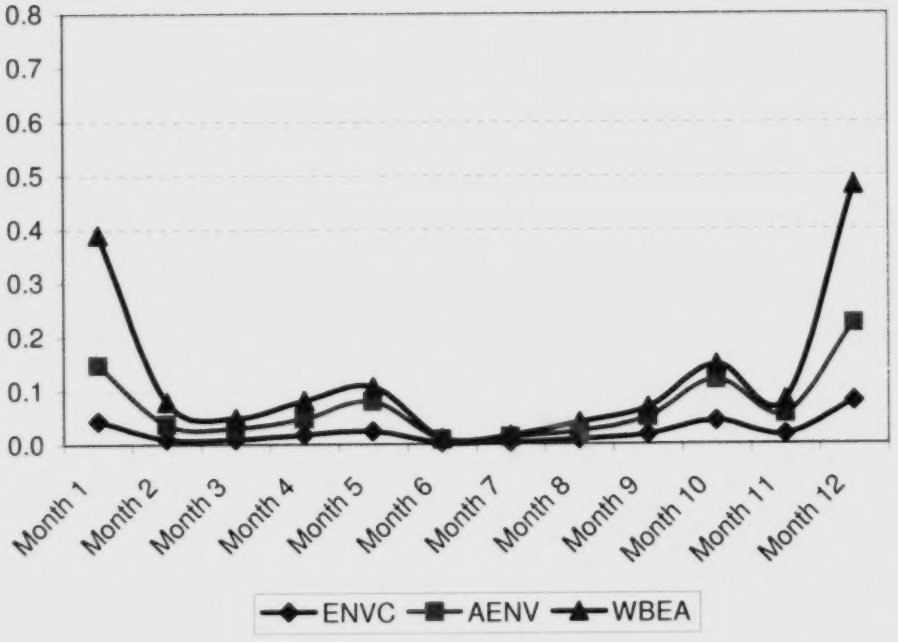


Figure 7. **Monthly nitrous acid (HNO_2) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg HNO_2/ha/month).**

(ENVC = Environment Canada method; AENV = Alberta Environment method; WBEA = Wood Buffalo Environmental Association method)

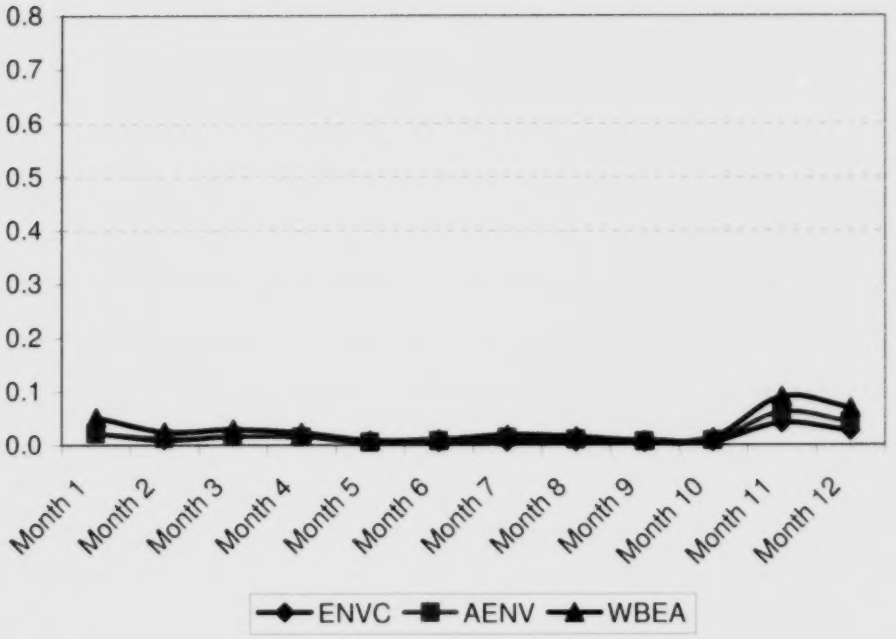


Figure 8. **Monthly nitrate (NO_3^-) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg NO_3^-/ha/month).**

(ENVC = Environment Canada method; AENV = Alberta Environment method; WBEA = Wood Buffalo Environmental Association method)

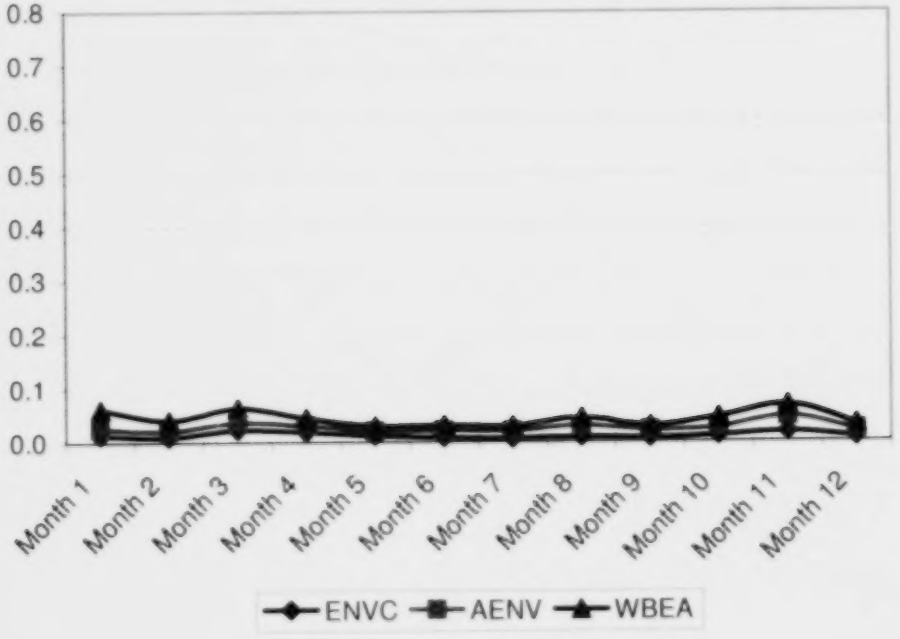


Figure 9. **Monthly ammonium (NH_4^+) dry deposition for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg NH_4^+/ha/month).**

(ENVC = Environment Canada method; AENV = Alberta Environment method; WBEA = Wood Buffalo Environmental Association method)

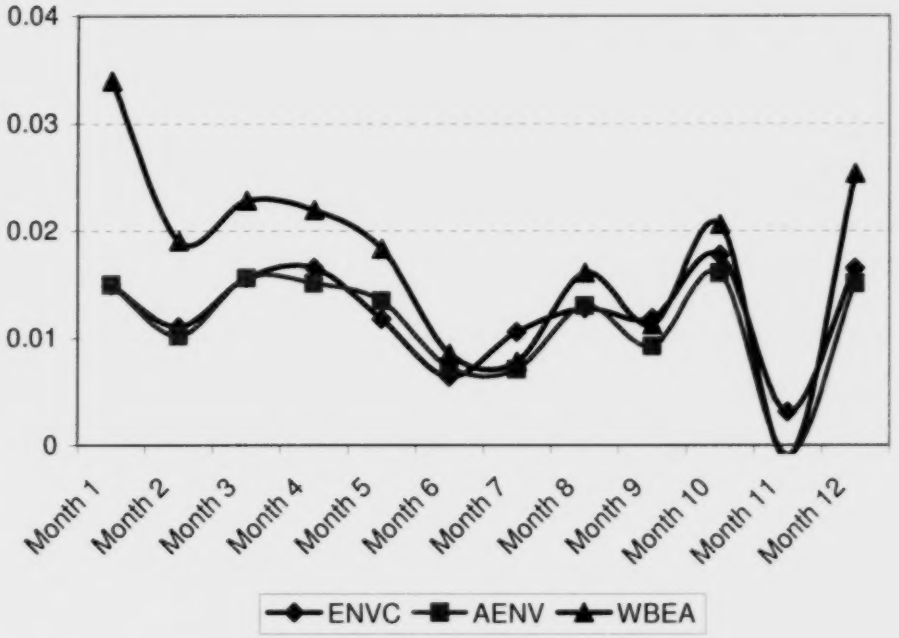


Figure 10. **Monthly potential acid input (PAI) values associated with dry species for the period January to December 2003 at WBEA Fort McKay air monitoring station AMS #1 (expressed in units of kg H^+/ha/month).**

(ENVC = Environment Canada method; AENV = Alberta Environment method; WBEA = Wood Buffalo Environmental Association method)

It is observed that ENVC model parameters have more boundary conditions (i.e. cut-off points and lower/upper limits) associated with their use (Appendix II) compared to the AENV model (Appendix I). Although not shown, it was observed that the AENV model had much greater variability associated with hourly model outputs. This may partially explain a net negative total PAI rate during the 11th month for the 2003 dataset. At this time the influence of assigning additional boundary conditions associated with AENV model input parameters on variability associated with model outputs is unknown. Further testing would be required to better understand whether this has an ability to improve AENV model performance relative to the ENVC model.

Annual total PAI rates associated with dry species at the Fort McKay site using the 2003 dataset were 0.15 kg H^+/ha/yr (ENVC method), 0.14 kg H^+/ha/yr (AENV method), and 0.20 kg H^+/ha/yr (WBEA method). The higher annual rate associated with dry species observed for the WBEA method relative to the other methods is entirely consistent with higher individual species deposition rates observed in Figures 4 to 9.

Limited data exist to enable comparisons of these results with other observations. Environment Canada (2004) reported on modeling activities in the 2004 Alberta-wide acid deposition assessment. Annual average concentrations and annual depositions of sulphur species were calculated for a 1° by 1° latitude-longitude grid area where the Fort McKay site is located using the REgional Lagrangian Acid Deposition (RELAD) model. Modeling was undertaken for the 1971-2000 period using 30 years of meteorological data and 1995 emissions.

Environment Canada (2004) presented data that indicate a 1971 to 2000 (30-yr) mean annual sulphur species dry deposition rate range of 0.06 to 0.08 kg H^+/ha/yr for a 1° by 1° latitude-longitude grid area where the Fort McKay site is located. Although these results are not directly comparable, annual total sulphur species dry deposition rates at the Fort McKay site using the 2003 dataset were 0.053 kg H^+/ha/yr (ENVC method), 0.044 kg H^+/ha/yr (AENV method), and 0.060 kg H^+/ha/yr (WBEA method).

RWDI (2004) reported historical measured and predicted NO_2 dry deposition rates for the Fort McKay site. RWDI (2004) reported an average measured NO_2 dry deposition rate of 0.17 kg H^+/ha/yr (2.33 kg N/ha/yr) for the 1999 to 2000 period. RWDI (2004) also reported an average modeled NO_2 dry deposition rate of 0.14 kg H^+/ha/yr (1.93 kg N/ha/yr) for the 1998 to 2002 period. Annual total NO_2 dry deposition rates at the Fort McKay site using the 2003 dataset were 0.10 kg H^+/ha/yr (ENVC method), 0.08 kg H^+/ha/yr (AENV method), and 0.12 kg H^+/ha/yr (WBEA method).

2.4.2 Comparison of Inference Methods

A general evaluation of model complexity and performance was recorded after work was completed with each inferential method for estimating dry deposition. A relative comparison of selective features of the three inference methods is presented in Table 3. Overall, it is the view of the report authors that the Environment Canada (ENVC) method is more sophisticated (complicated) given that it has the greatest number of input

parameter requirements. Although not shown, it also required making a number of additional assumptions for some of the input parameters before modeling could be performed.

Table 3. Relative comparison of selective features of three inference methods for estimating dry deposition.

	ENVC	AENV	WBEA
Number of Parameters	18	9	7
Relative level of complexity	High	Medium	Low
Relative computing time requirements	High	Low	Low
Method for calculating R_a	Resistance model	Resistance model	Empirical equation
Method for calculating R_b	Resistance model	Resistance model for gas and empirical constant for particles	Resistance model for gas and empirical constant for particles
Method for calculating R_c	Resistance model	Empirical constant	Empirical constant
Major assumptions required	Meteorological data: hourly precipitation obtained from daily totals in vague way Particle mass distribution was assumed	n/a	n/a
Number of land use categories (LUCs)	26	8	8
Seasons	Function of latitude and month	Function of month, 4 seasons total	Function of month
Number of gas species	31	4	4
Assumptions for particulate species	Based on distribution assumptions	7	7
Wetness correction	Corrected based on rain and dew condition, respectively	Time weighted by combined surface wetness and related humidity conditions	Corrected by combined surface wetness and related humidity conditions
Basis for leaf area index (LAI)	Function of LUC and season	n/a	n/a
Basis for surface roughness	Function of LUC and Season	Function of wind speed and wind direction deviation	n/a
Basis for stability condition	Temperature difference with temperature gradient correction	Temperature difference	Day vs. night (unstable vs. stable assumption)

ENVC = Environment Canada method, AENV = Alberta Environment method,
WBEA = Wood Buffalo Environmental Association method
n/a = not applicable

The Alberta Environment (AENV) method provided comparative results to the ENVC method based on the 2003 Fort McKay dataset. This method is less complicated compared to the ENVC method, and it requires less input data and computing time. Finally, the Wood Buffalo Environmental Association (WBEA) method is simple and straight-forward to program. However as discussed previously, this method yielded higher monthly deposition rates for most species modeled using the 2003 dataset.

Although a limited one-year dataset was available to evaluate these models, it is the view of the report authors that the AENV method offers a practical choice for routine computation of sulphur and nitrogen species dry deposition in Alberta. Further testing using different datasets elsewhere in Alberta is recommended to support this. If the ENVC method can be shown to provide comparative results to the AENV method using different datasets elsewhere in Alberta, it offers a logical choice for periodic use as a check on the AENV method.

2.4.3 Relationships of Dry Deposition for Sulphur and Nitrogen Species

Contributions of SO_2 and NO_2 deposition in total sulphur and nitrogen species deposition at the Fort McKay site were examined for the one-year dataset. Annual sulphur and nitrogen species deposition data were analyzed to determine the ratio of SO_2 deposition to total sulphur species deposition and of NO_2 deposition to total nitrogen species deposition. These results are presented in Table 4 (SO_2 to total S species deposition ratio) and Table 5 (NO_2 to total N species deposition ratio), respectively.

Table 4. Ratio of annual SO_2 deposition to total sulphur species deposition at WBEA Fort McKay air monitoring station during 2003.

Method	SO_2	SO_4^{2-}	SO_2/S_{tot}
	kg S/ha/yr	kg S/ha/yr	2.4.3.1 Ratio
ENVC	1.489	0.101	**0.94**
AENV	0.975	0.222	**0.82**
WBEA	1.197	0.361	**0.77**

Note: $\frac{SO_2}{S_{tot}}$ Ratio = $\frac{SO_2}{SO_2 + SO_4^{2-}}$

ENVC = Environment Canada method
AENV = Alberta Environment method
WBEA = Wood Buffalo Environmental Association method

Results presented in Table 4 and 5 using the Alberta Environment method (AENV) are discussed here because previous work by WBK (2008) used the same method to estimate ratios at another acid deposition monitoring site in Alberta – Beaverlodge. Estimates of

annual S species deposition for the Fort McKay site indicate that about 82% is in the form of gaseous SO_2 with the remainder as particulate sulphate (18%).

WBK (2008) reported on annual deposition loadings of S and N species during 1998 to 2002 at a former Alberta Environment Beaverlodge acid deposition monitoring site. The station was located west of Grande Prairie at an Agriculture and Agri-food Canada Research Farm. Estimates of annual S species deposition (Table 6) consistently showed that about 80% was in the form of gaseous SO_2 with the remainder as particulate sulphate. These data compare well with that observed at Fort McKay during 2003 (82%).

Table 5. Ratio of annual NO_2 deposition to total nitrogen species deposition at WBEA Fort McKay air monitoring station during 2003.

Method	NO_2	HNO_3	HNO_2	NO_3^-	NH_4^+	NO_2/N_{tot}
	Kg N/ha/yr	kg N/ha/yr	kg N/ha/yr	kg N/ha/yr	kg N/ha/yr	2.4.3.2 Ratio
ENVC	1.368	0.430	0.083	0.038	0.112	**0.67**
AENV	1.132	0.524	0.250	0.051	0.250	**0.51**
WBEA	1.632	0.850	0.463	0.082	0.404	**0.48**

Note: $\frac{NO_2}{N_{tot}}$ Ratio = $\frac{NO_2}{NO_2 + HNO_3 + HNO_2 + NH_4^+ + NO_3^-}$

ENVC = Environment Canada method
AENV = Alberta Environment method
WBEA = Wood Buffalo Environmental Association method

Estimates of annual N species deposition at the Fort McKay site showed that about 51% was from NO_2 with the remainder as HNO_3 and HNO_2 (35%) and particulate ammonium and nitrate (<14%). Estimates of annual N species deposition at the Beaverlodge site (Table 7) showed that about 35 to 50% was from NO_x ($NO + NO_2$) with the remainder as HNO_3 and HNO_2 (~40 to 60%) and particulate ammonium and nitrate (<10%) (WBK, 2008). Again, results for the Beaverlodge site on the same order as that observed at the Fort McKay site.

WBK (2008) reported on work of Peake and Davidson (1990) related to estimated annual dry deposition of N species (NO_x, HNO_2, HNO_3, and NO_3^-) in the south western region of Alberta. This region stretches east from the Great Divide of the Rocky Mountains to the plains of southern Alberta, 80 km east of Calgary, as discussed by Peake and Davidson (1990). These estimates were based upon measurements made at Crossfield east and west, and Fortress Mountain monitoring sites during 1985 to 1987 as part of the Alberta Government/Industry Acid Deposition Research Program (ADRP). Using data reported by Peake and Davidson (1990). WBK (2008) estimated that about 32% of N deposition was from NO_x ($NO + NO_2$) with the remainder as nitric and nitrous acid (~63%) and particulate nitrate (~5%).

Table 6. **Ratio of annual SO_2 deposition to total sulphur species deposition at Beaverlodge, Alberta (after WBK, 2008).**

	SO_2	SO_4^{2-}	SO_2/S_{tot}
Year	kg S/ha/yr	kg S/ha/yr	2.4.3.3 Ratio
1998	0.368	0.083	**0.82**
1999	0.305	0.072	**0.81**
2000	0.294	0.064	**0.82**
2001	0.317	0.069	**0.82**
2002	0.317	0.072	**0.81**

Note: $\frac{SO_2}{S_{tot}}$ Ratio = $\frac{SO_2}{SO_2 + SO_4^{2-}}$

Bytnerowicz et al. (1999) as cited in Bytnerowicz et al. (2005) reported that HNO_3 typically provides more than 60% of all dry-deposited N species in mixed conifer forests of the Los Angeles Basin mountain range of California.

Table 7. **Ratio of annual NO_x deposition to total nitrogen species deposition at Beaverlodge, Alberta (after WBK, 2008).**

	NO_x	HNO_3	HNO_2	NO_3^-	NH_4^+	NO_x/N_{tot}
Year	Kg N/ha/yr	kg N/ha/yr	kg N/ha/yr	kg N/ha/yr	kg N/ha/yr	2.4.3.4 Ratio
1998	0.617	0.370	0.097	0.030	0.077	**0.52**
1999	0.556	0.482	0.051	0.034	0.060	**0.47**
2000	0.551	0.412	0.064	0.029	0.054	**0.50**
2001	0.572	0.600	0.098	0.035	0.050	**0.42**
2002	0.679	0.952	0.229	0.041	0.040	**0.35**

Note: NO_x/N_{tot} Ratio = $\frac{NO_x}{NO_x + HNO_3 + HNO_2 + NH_4^+ + NO_3^-}$

3.0 FINDINGS AND RECOMMENDATIONS

1. Complete sulphur and nitrogen gaseous and particulate species and meteorological data for a one-year period (2003) from the Wood Buffalo Environmental Association Fort McKay air monitoring station were evaluated using the three methods. All three methods showed a similar ability to represent variation in dry deposition rates for individual species from month to month.

2. The WBEA method yielded higher monthly deposition rates for most species modeled (SO_4^{2-}, NO_2, HNO_3, HNO_2, and NH_4^+) compared to the AENV and ENVC methods. The WBEA method also yielded higher potential acid input (PAI) values associated with dry species compared to the AENV and ENVC methods during winter and spring. The WBEA method gave similar PAI values associated with dry species during summer and fall. A simpler computational approach for aerodynamic and surface resistance terms in the WBEA method may partially explain differences observed during winter and spring. Further testing would be required to better understand whether this is the case.

3. Annual total PAI associated with dry species for 2003 was 0.14 kg H^+/ha/yr (AENV method), 0.15 kg H^+/ha/yr (ENVC method), and 0.20 kg H^+/ha/yr (WBEA method). The higher annual rate associated with dry species observed for the WBEA method relative to other methods is consistent with higher monthly deposition rates for individual species. While the AENV and ENVC methods yielded comparable monthly PAI values associated with dry species, it is observed that ENVC input parameters have more boundary conditions (i.e. cut-off points and lower/upper limits) associated with their use compared to AENV input parameters.

4. The ENVC method is more complicated given that it has the greatest number of input parameter requirements. A number of additional assumptions for some of the input parameters are also required before modeling can be performed. The AENV method provided comparative results to the ENVC method. The AENV method is less complicated compared to the ENVC method, and it requires less input data and computing time. The WBEA method is simple and straight-forward to use. However, this method yielded higher monthly deposition rates for most species modeled compared to the other methods using the 2003 dataset.

5. The dataset used to evaluate the methods was short – one year – and month to month variation or lack of variation in species deposition rates observed using each method does not necessarily provide an indication of what may happen in other years. Although only a one-year dataset was available for evaluation, results support that the AENV method offers a practical choice for routine computation of sulphur and nitrogen species dry deposition in Alberta. Further testing using different datasets elsewhere in Alberta is recommended to support

this. If the ENVC method can be shown to provide comparable results to the AENV method using different datasets, it would offer a logical choice for periodic use as a check on the AENV method.

6. Evaluation of contributions of SO_2 and NO_2 deposition in total sulphur and nitrogen species deposition at the Fort McKay site indicated that about 82% is in the form of gaseous SO_2 with the remainder as particulate SO_4^{2-} (18%). These results are comparable to annual deposition loadings of sulphur species during 1998 to 2002 at the former Alberta Environment Beaverlodge acid deposition monitoring site (80% in the form of gaseous SO_2 and 20% as particulate SO_4^{2-}).

   Estimates of annual nitrogen species deposition at the Fort McKay site indicated that ~51% was from NO_2 with the remainder as HNO_3 and HNO_2 (35%) and particulate NH_4^+ and NO_3^- (<14%). Estimates of annual nitrogen species deposition at the Beaverlodge site during 1998 to 2002 showed that about 35 to 50% was from NO and NO_2 with the remainder as HNO_3 and HNO_2 (40 to 60%) and particulate NH_4^+ and NO_3^- (<10%).

7. Future work evaluating these inference methods should consider the influence of assigning additional boundary conditions to AENV model input parameters on variability associated with model outputs. Specifically, assigning boundary conditions to AENV input parameters consistent with default ENVC model assumptions should be investigated to better understand whether these changes have the ability to improve AENV model performance relative to the ENVC model.

4.0 REFERENCES

Brook, J., Zhang, L., Di Giovannic, F., and Padro, J. 1999a. Description and evaluation of a model of deposition velocities for routine estimates of air pollutant dry deposition over North America. Part I: model development. *Atmos. Environ.*, **33**: 5037-5051.

Brook, J., Zhang, L., Li, Y., and Johnson, D.. 1999b. Description and evaluation of a model of deposition velocities for routine estimates of air pollutant dry deposition over North America. Part II: review of past measurements and model results. *Atmos. Environ.*, **33**: 5053-5070.

Bytnerowicz, A., Sanz, M., Arbaugh, M., Padgett, P., Jones, D., and Davila, A. 2005. Passive sampler for monitoring ambient nitric acid (HNO_3) and nitrous acid (HNO_2) concentrations. *Atmos. Environ.*, **39**: 2655-2660.

Bytnerowicz, A., Tausz, M., Alonso, R., Jones, D., Johnson, R., and Grulke, N. 2002a. Summer-time distribution of air pollutants in Sequoia National Park, California. *Environ. Pollut.*, **188**: 187-203.

Bytnerowicz, A., Parker, D., and Padgett, P. 2002b. Vertical distribution of ozone and nitric acid vapor on the Mammoth Mountain, Eastern Sierra Nevada, California. *Sci. World J.*, **2**: 1-9.

Bytnerowicz, A., Padgett, P., Arbaugh, M., Parker, D., and Jones, D. 2001. Passive sampler for measurements of atmospheric nitric acid vapor (HNO_3) concentrations. *Sci. World J.*, **1**: 815-822.

Canadian Oil Sands Trust (COST). 2006. Canadian Oil Sands Trust, Calgary, AB. Available at: http://www.cos-trust.com/asset/ (accessed February 2006).

Cheng, L., Bates, D.L., and Myrick, B. 2001. Acidic Deposition Monitoring and Calculations in Alberta, Draft 5. Alberta Environment, Edmonton, AB. 28 pp.

Cheng, L., McDonald, K., Fox, D., and Angle, R. 1997, Total Potential Acid Input in Alberta. Alberta Environmental Protection, Edmonton, AB. 27 pp.

Clarke, J.F., Edgerton, E.S., and Martin, B.E. 1997. Dry deposition calculations for the Clean Air Status and Trends Network. *Atmos. Environ.*, **31**: 3667-3678.

EPCM Associates Ltd. (EPCM). 2002. Operational Manual for TEEM DEP Model – Estimation of Dry Acidic Deposition at TEEM Passive Monitoring Sites. Report prepared for Wood Buffalo Environmental Association Terrestrial Environmental Effects Monitoring (TEEM) Committee, Fort McMurray, AB. April 2002. 13 pp

EPCM. 2000. Evaluation of Passive Sampling Systems at TEEM Jack Pine Monitoring sites. Part II. Dry Deposition of SO2. Report prepared for Wood Buffalo Environmental Association Terrestrial Environmental Effects Monitoring (TEEM) Committee, Fort McMurray, AB. 13 November 2000. 24 pp.

Erisman, J.W., Van Pul, A., and Wyers, P. 1994. Parameterization of surface resistance of the quantification of atmospheric deposition of acidifying pollutants and ozone. *Atmos. Environ.*, **28**: 2595-2607.

Environment Canada (ENVC). 2004. 2004 Canadian Acid Deposition Science Assessment. En4-46/2004E-MRC. Environment Canada, Meteorological Service of Canada (MSC), Ottawa, ON. Available at: http://www.msc-smc.ec.gc.ca/saib/acid/acid_e.html (accessed January 2006).

Giorgi, F. 1988. Dry deposition velocities of atmospheric aerosols as inferred by applying a particle dry deposition parameterization to a general circulation model. *Tellus*, **40B**: 23-41.

Hicks, B.B., Baldoechi, D.D., Meyers T.P., Hosker Jr R.P., and Matt, D.R. 1987. A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. *Wat. Air Soil Pollut.*, **26**: 311-330.

Hicks, B.B. 1982. Critical Assessment Document on Acid Deposition (Chapter VII-Dry Deposition). ATDL Contribution File No. 81/24. Atmospheric Turbulence and Diffusion Laboratory, National Oceanic and Atmospheric Administration, Oak Ridge, TN.

Howard, P.H. and Meylan, W.M. 1997. Handbook of Physical Properties of Organic Chemicals. CRC Lewis Publishers, Boca Raton, FL.

Lovett, G.M. 1994. Atmospheric deposition of nutrients and pollutants in North America: an ecological perspective. *Ecol. Appl.*, **4**: 629-650.

Padro, J. 1996. Summary of ozone dry deposition velocity measurements and model estimates over vineyard, cotton, grass and deciduous forest in summer. *Atmos. Environ.*, **30**: 2363-2369.

Padro, J., den Hartog, G., and Neumann, H.H. 1991. An investigation of the ADOM dry deposition module using summertime O_3 measurements above a deciduous forest. *Atmos. Environ.*, **25**: 1689-1704.

Peake, E. and Davidson, C.I. 1990. Wet and dry deposition of air pollutants in Alberta. In: Acidic Deposition: Sulphur and Nitrogen Oxides, A.H. Legge and S.V. Krupa (ed.). Lewis Publishers, Chelsea, MI. pp. 381-412.

Peters, K. and Eiden, R. 1992. Modelling the dry deposition velocity of aerosols particles to a Spruce forest. *Atmos. Environ.*, **26**: 2555-2564.

Pleim, J., Venkatram, A., and Yamartino, R. 1984. ADOM/TADAP Model Development Program. ERT P-B980-520. Prepared for OME, AES of Canada and the Umweltbundesamt, West Germany.

Ruijgrok, W., Tieben, H., and Eisinga, P., 1997. The dry deposition of particles to a forest canopy: a comparison of model and experimental results. *Atmos. Environ.*, **31**: 399-415.

RWDI West Inc. (RWDI). 2004. NO_x Dispersion and Chemistry Assumptions in the CALPUFF Model. Draft report prepared for NO_xSO_x Management Working Group, Cumulative Effects Management Association, Fort McMurray, AB. October 2004.

Sander, R. 1999. Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (version 3). Available at: http://www.mpchmainz.mpg.de/~sander/res/henry.html.

Slinn, W.G.N. 1982. Predictions for particle deposition to vegetative surfaces. *Atmos. Environ.*, **16**: 1785-1794.

US Environmental Protection Agency (EPA). 2001. Frequently Asked Questions About Acid Deposition. EPA-453/R-01-009. US EPA Office of Air Quality, Research Triangle Park, NC 27711. September 2001.

Wesely, M.L. and Hicks, B.B. 2000. A review of the current status of knowledge on dry deposition. *Atmos. Environ.*, **34**: 2261-2282.

Wesley, M.L. and Hicks, B.B. 1977. Some factors that affect the deposition rates of sulphur dioxide and similar gases on vegetation. *J. Air Poll. Cont. Assoc.*, **27**: 1110-1116.

Wesely, M.L., Cook, D.R., Hart, R.L., and Speer, R.R. 1985. Measurements and parameterization of particle sulphur deposition over grass. *J. Geophysical Res.*, **90**: 2131-2143.

WBK & Associates Inc. (WBK). 2008. Review and Assessment of Methods for Monitoring and Estimating Dry Deposition in Alberta. Report prepared for Alberta Environment, Edmonton, AB. June 2008. 54 pp.

Zhang, L., Brook, J., and Vet, R. 2003a. Evaluation of a non-stomatal resistance parameterization for SO_2 dry deposition. *Atmos. Environ.*, **37**: 2941–2947.

Zhang, L., Brook, J., and Vet, R. 2003b. A revised parameterization for gaseous dry deposition in air-quality models. *Atmos. Chem. Phys. Discuss.*, **3**: 1777-1804.

Zhang, L., Moran, M., Makar, P., Brook, J., and Gong, S. 2002a. Modelling gaseous dry deposition in AURAMS – A Unified Regional Air-quality Modelling System. *Atmos. Environ.*, **36**: 537–560.

Zhang, L., Brook, J., and Vet, R. 2002b. On ozone dry deposition with emphasis on non-stomatal uptake and wet canopies. *Atmos. Environ.* **36**: 4787–4799.

Zhang, L., Gong, S.L., Padro, J., and Barrie, L. 2001a. A size-segregated particle dry deposition scheme for an atmospheric aerosol module. *Atmos. Environ.*, **35**: 549-560.

Zhang, L., Moran, M.D., Makar, P.A., Brook, J.R., and Gong, S. 2001b. Modelling gaseous dry deposition in AURAMS: a unified regional air-quality modelling system. *Atmos. Environ.*, **36**: 537-560.

APPENDIX I

Alberta Environment Calculation Methods for Gases and Particulates

(after Cheng et al., 2001)

Parameters:

PAI	Potential Acid Input (kg H^+/ha/yr)
[X]	concentration of X chemical species deposited (kg/ha/yr)
F	dry deposition flux ($\mu g/m^2/s$)
V_d	deposition velocity (m/s)
C	concentration ($\mu g/m^3$)
R_a	aerodynamic resistance (s/m)
R_b	boundary-layer resistance (s/m)
R_c	surface resistance (s/m)
k	von Karman constant (0.4)
u^*	friction velocity (m/s)
z	reference height (10 m)
z_0	surface roughness length (m)
ψ	integrated stability correction term
L	Monin-Obukhov length scale
u	wind speed (m/s)
σ_θ	standard deviation of wind direction (rad)
R_i	Bulk Richardson number
g	gravitational acceleration (9.81 m/s^2)
T_d	temperature difference between 10 and 2 m ($T_{10} - T_2$)
T_2	temperature at 2 m (Kelvin)
H	sensible heat flux (w/m^2)
B	defined equation described herein
η	dynamic viscosity of air (18.0×10^{-6} N-s/m^2 at 1 atm and 25°C)
ρ	density of air (1.18 kg/m^3 at 1 atm and 25°C)
D	diffusion coefficient of the substance of interest (cm^2/s)
Pr	Prandtl number for air (0.72)
$\eta/\rho D$	Schmidt number
RH	relative humidity
SW	soil wetness

Equations:

$$\mathbf{PAI_{dry}} = \frac{[SO_2]}{64} + \frac{[NO_2]}{46} + \frac{[HNO_2]}{47} + \frac{[HNO_3]}{63} + 2\frac{[SO_4^{2-}]}{96} + \frac{[NO_3^-]}{62} + \frac{[NH_4^+]}{18} - \left(\frac{[K^+]}{39} + \frac{[Na^+]}{23} + 2\frac{[Ca^{2+}]}{40} + 2\frac{[Mg^{2+}]}{24}\right)$$

deposition concentrations units in kg/ha/yr

$$\mathbf{F} = V_d C$$

$$\mathbf{V_d} = \frac{1}{(R_a + R_b + R_c)}$$

Summary of Species Specific Deposition Velocity Formulae:

$$V_{d\{SO_2\}} = \frac{1}{R_a + R_{b\{SO_2\}} + R_{c\{SO_2\}}}$$

$$V_{d\{NO_2\}} = \frac{1}{R_a + R_{b\{NO_2\}} + R_{c\{NO_x\}}}$$

$$V_{d\{HNO_3\}} = \frac{1}{R_a + R_{b\{SO_2\}}}$$

$$V_{d\{HNO_2\}} = \frac{1}{R_a + R_{b\{HNO_2\}}}$$

R_c is treated as being negligible for nitric and nitrous acid.

$$V_{d\{SO_4^{2-}, NH_4^+\}} = \frac{1}{R_a + R_{b\{SO_4^{2-}\}}}$$

$$V_{d\{NO_3^-, Ca^{2+}, Mg^{2+}, K^+, Na^+\}} = \frac{1}{R_a + (0.5 \times R_{b\{SO_4^{2-}\}})}$$

Aerodynamic Resistance:

$$R_a = \frac{1}{ku^*}\left\{\ln\frac{z}{z_0} - \psi\left(\frac{z}{L}\right)\right\}$$ (R_a is infinite and $V_d = 0$ when u and T_d are zero)

$u^* = \frac{u\sigma_\theta}{1.9}$ (this relationship is used as an initial estimate of u^* to calculate z_0, a more precise value of u^* is calculated after z_0 is obtained – refer to below)

$z_0 = z\, e^{-\left(\frac{0.4u}{u^*}\right)}$ (calculated as a monthly average using data where the wind speed is >6 m/s)

$$R_i = \frac{gzT_d}{T_2 u^2}$$

A more precise value of u^* calculated after z_0 is obtained (based on atmospheric conditions):

Stable conditions $\mathbf{R_i} > 0$ $$u^* = ku\left\{\ln\left(\frac{z}{z_0}\right)(1 + 4.7Ri)\right\}^{-1}$$

Unstable conditions $\mathbf{R_i} < 0$ $$u^* = \frac{ku}{\ln\left(\frac{z}{z_0}\right)\sqrt{1 - \left\{\frac{9.4Ri}{1 + (7.4B)}\right\}}}$$

Neutral conditions $\mathbf{R_i} = 0$ $$u^* = \frac{ku}{\ln\left(\frac{z}{z_0}\right)}$$

Calculation of ψ (based on atmospheric conditions):

Stable conditions $$\psi = -\frac{5z}{L} \qquad \text{where } \mathbf{L} = \frac{T_2 u^{*3}}{kHg}$$

Unstable conditions $$\psi = 2\ln\left\{\frac{1}{2}\left(1 + \sqrt{1 - \frac{15z}{L}}\right)\right\}$$

Neutral conditions $\psi = 0$

Calculation of H (based on atmospheric conditions):

Neutral and *Stable conditions* $$\mathbf{H} = \left\{\frac{uT_d}{0.74}\right\}\left\{\frac{k}{\ln\left(\frac{z}{z_0}\right)}\right\}^2\left\{\frac{1}{(1 + 4.7Ri)^2}\right\}$$

Unstable conditions

$$\mathbf{H} = \left\{\frac{uT_d}{0.74}\right\}\left\{\frac{k}{\ln\left(\frac{z}{z_0}\right)}\right\}^2\left\{1-\frac{9.4Ri}{(1+5.3B)}\right\}$$

where $\mathbf{B} = 9.4\left[\frac{k}{\ln\left(z/z_0\right)}\right]^2\left[|R_i|\frac{z}{z_0}\right]^{1/2}$

Boundary Layer Resistance:

R_b (gases):

$$R_b = R_b = \frac{2}{ku_*}\left(\frac{\eta}{\rho D}\times\frac{1}{\mathrm{Pr}}\right)^{2/3}$$

$$R_b = \frac{7.22}{u_*} \text{ for } SO_2 \text{ and } HNO_3$$

$$R_b = \frac{6.18}{u_*} \text{ for } NO_2$$

$$R_b = \frac{6.09}{u_*} \text{ for } HNO_2$$

R_b (particulates):

R_b values for particulate sulphate are obtained from scientific literature for daytime and nighttime as a function of surface type and weighted according to average day length for each month at a mid-Alberta latitude location (54°N latitude) after Cheng and Angle (1993) as cited in Cheng et al. (2001).

Boundary-Layer Resistance (s/cm) for Particulate Sulphate, Day Length Weighted Averages at 54°N Latitude for the Middle of Each Month.

Surface Type	Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May)		Summer (Jun, July, Aug)		Autumn (Sep, Oct, Nov)	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Deciduous Forest	16.9	0	5.4	0	1.3	0	3.2	0
Coniferous Forest	2.5	0	2.7	0	1.9	0	2.3	0
Wetland/Swamp*	20.4	0	3.8	0	2.6	0	3.2	0
Grassland*	20.4	0	5.6	0	3.9	0	4.7	0
Cropland*	20.4	0	9.0[‡]	0	3.9	0	7.9[‡]	0
Urban[§]	33.9	0	10.9	0	2.6	0	6.3	0

Open Water	0	0	0	0	0	0	0	0
Snow/Ice	20.4	0	-	-	-	-	-	-

* in winter, wetland, grassland, and cropland treated as a snow surface. † bare soil and active growth.
‡ bare soil and senescent growth. § consists of a mixture of deciduous forest and buildings.

Day length Weighted Seasonal Average R_b = $\frac{day\ length}{24hrs}\left(R_{b\ day}\right)+\left(1-\frac{day\ length}{24hrs}\left(R_{b\ night}\right)\right)$

Day length = $0.133\left\{\cos^{-1}\left(-\tan(55^{\circ})\times\tan(Solar\ Declination)\right)\right\}$

Solar Declination = $23.45\left\{\sin\left(\frac{360\times(284+Julian\ Day)}{365}\right)\right\}$

Surface Resistance:

Bulk surface resistance values are used from literature as a function of surface type, surface wetness, and incident radiation. Day length weighted average R_c values for SO_2 and NO_2 are used from Voldner et al (1986), Arrit et al (1987) and Walcek et al (1986) as cited in Cheng et al. (2001):

Day Length Weighted Averages Bulk Surface Resistance (s/cm) for Sulphur Dioxide (SO_2):

Surface Type	Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May)		Summer (Jun, July, Aug)		Autumn (Sep, Oct, Nov)	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Deciduous Forest	10	10	4.7	0	3.5	0	7.9	0.4
Coniferous Forest	5	5	4.1	0	3.5	0	4.9	0.2
Wetland/Swamp*	7	1	0.5	0	0.7	0	1	0.1
Grassland*	7	1	1	0	1.3	0	2	0.1
Cropland*	7	1	0‡	0	2	0	2‡	0.1
Urban§	10	2	10	0	10	0	10	0.1
Open Water	0	0	0	0	0	0	0	0
Snow/Ice	7	1	-	-	-	-	-	-

* in winter, wetland, grassland, and cropland treated as a snow surface. † bare soil and active growth.
‡ bare soil and senescent growth. § consists of a mixture of deciduous forest and buildings.

Day Length Weighted Averages Bulk Surface Resistance (s/cm) for Nitrogen Dioxide (NO_2):

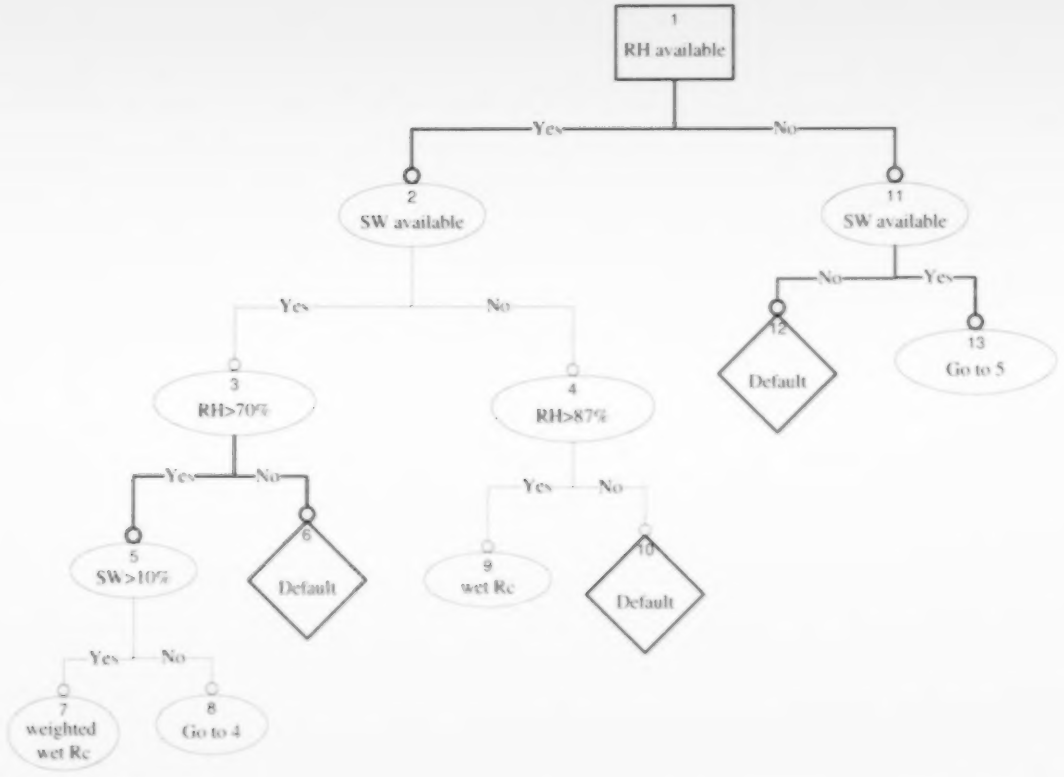
Surface Type	Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May)		Summer (Jun, July, Aug)		Autumn (Sep, Oct, Nov)	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Deciduous Forest	20.0	70.0	3.3	70.0	2.2	70.0	4.7	70.0

Coniferous Forest	10.0	70.0	2.7	70.0	2.2	70.0	3.3	70.0
Wetland/Swamp*	50.0	70.0	12.1	70.0	11.5	70.0	12.9	70.0
Grassland*	50.0	70.0	3.3	70.0	3.3	70.0	6.6	70.0
Cropland*	50.0	70.0	3.3[†]	70.0	4.6	70.0	7.9[‡]	70.0
Urban[§]	10.0	70.0	10.0	70.0	10.0	70.0	10.0	70.0
Open Water	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0
Snow/Ice	50.0	70.0	-	-	-	-	-	-

* in winter, wetland, grassland, and cropland treated as a snow surface. † bare soil and active growth.
‡ bare soil and senescent growth. § consists of a mixture of deciduous forest and buildings.

R_c (HNO_3): 10 s/m (for all seasons and all surfaces)
R_c (HNO_2): 10 s/m (for all seasons and all surfaces)
R_c (NH_3): 28 s/m (dry conditions)
9 s/m (wet conditions)
201 s/m (when T_2<0°C)
R_c (particulates): 0 s/m

R_c is calculated based on surface wetness criteria, such that it either represents a "total dry condition," "total wet condition," or "weighted wet condition" using the following flowchart, and relative humidity (RH) and surface wetness (SW) criteria:



Adapted from Bates (1996)

Default = R_c value for dry conditions
Wet R_c = R_c value for wet conditions
Weighted Wet R_c = Time weighted wet R_c

Time weighted wet R_c = $$\left(\frac{SW}{100} \times wet\ Rc\right) + \left[\left(1 - \frac{SW}{100}\right) \times dry\ Rc\right]$$

Calculation of V_d in the absence of meteorological data:

Missing hourly meteorological data are treated in the following manner:

- 1 hour of meteorological data missing → the average resistance of the hours before and after are used to represent the missing hour
- consecutive hours of meteorological data missing → each hour's calculated median resistance for the month is used to represent the missing hours

APPENDIX II

Environment Canada Calculation Methods for Gases and Particulates

(after Brooks, 1999a, 199b; Zhang et al., 2003a, 2003b, 2002a, 2002b, 2001a, and 2001b)

Parameters (for gases):

V_d:	deposition velocity (m/s)
R_a:	aerodynamic resistance (s/m)
R_b:	boundary-layer resistance (s/m)
R_c:	surface resistance (s/m)
k:	von Karman constant (0.4)
u_*:	friction velocity (m/s)
u:	horizontal wind speed at reference height (m/s)
L:	Monin-Obukhov length
H:	sensible heat flux
z:	reference height (10m)
z_0:	surface roughness length (m)
ψ_H:	stability function
Ri:	Bulk Richardson number
g:	gravitational acceleration (9.81 m/s^2)
T_2:	temperature at reference height (°K)
T_{2p}:	potential temperature at reference height (°K)
T_s:	surface temperature (°K)
T_d:	temperature difference (°K)
P:	surface pressure (kPa)
T_{avg}:	temperature average, $T_{avg} = (T_{2p} + T_s)/2$
SR:	solar radiation (w/m^2)
RH:	relative humidity (%)
$Prec$:	precipitation (mm/hour)
$FCLD$:	fraction of cloud covering (%)
$\cos\theta$:	cosine of solar zenith angle
$\cos\alpha$:	cosine of sun/leaf angle, set as 0.5
Di:	molecular diffusivity
Dv:	water diffusivity
Vi:	thermal diffusivity
MW:	Molecular Weight, $MW_{air} = 29$

W_{st}:	fraction of stomatal blocking under wet conditions
R_{st}:	stomatal resistance
R_m:	mesophyll resistance (dependent only on chemical species)
R_{ac}:	in-canopy aerodynamic resistance (not chemical species-dependent)
R_g:	ground resistance (scaled from SO_2 and O_3's R_g)
R_{cut}:	cuticle uptake resistance (scaled from SO_2 and O_3's R_{cut})
$G_s(PAR)$:	unstressed leaf stomatal conductance
PAR:	Photosynthetic Active Radiation
$f(T)$:	conductance-reducing effects of air temperature T (°C)
$f(D)$:	conductance-reducing effects of water-vapour-pressure deficit D
D:	water-vapour-pressure deficit
$f(\psi)$:	conductance-reducing effects of water stress ψ
ψ:	water stress
ψ_{c1} and ψ_{c2}:	leaf-water-potential dependency
$E^*(T)$:	saturation water vapour pressure (kPa) at air temperature T (°K)
E:	ambient water vapour pressure (kPa)
f_{snow}:	snow cover fraction
Sd:	snow depth (cm)
Sd_{max}:	maximum snow depth (cm)
R_{cutw0}:	reference values of wet cuticle resistance, see Table 1 for $R_{cutw0}(O_3)$
$R_{cutw0}(SO_2)$:	50 s/m or 100 s/m for rain or dew conditions, respectively
R_{cutd0}:	reference values of dry cuticle resistance, see Table 1
LAI:	Leaf Area Index
LUC:	Land Use Category (26 LUCs in gas model)

Deposition Velocity:

$$V_d = \frac{1}{R_a + R_b + R_c}$$

Aerodynamic Resistance (for surfaces other than water/lake):

ENVC adapts the Acid Deposition and Oxidant Model (ADOM) formulated by Pleim et. al. (1984) and further investigated by Padro et al. (1990).

$$R_a = \frac{1}{ku_*}\left[0.74\ln(z/z_0) - \psi_H\right], \text{ with a lower limit of 5 and upper limit of 1000}$$

Friction velocity:

$$u_* = \begin{cases} \dfrac{ku}{\ln\left(\dfrac{z}{z0}\right)(1+4.7Ri)} & Stable,\ Ri > 0 \\ \dfrac{ku}{\ln\left(\dfrac{z}{z0}\right)}\sqrt{1-\dfrac{9.4Ri}{1+7.4\left[k/\ln\left(\dfrac{z}{z0}\right)\right]^2\sqrt{|Ri|}}} & Unstable,\ Ri < 0 \end{cases}$$

Stability function:

$$\psi_H = \begin{cases} -4.7\dfrac{z}{L} & stable,\ 0 < \dfrac{z}{L} < 1 \\ 0.74 \times 2\ln\left\{\dfrac{1+\sqrt{1-9\dfrac{z}{L}}}{2}\right\} & unstable,\ -1 < \dfrac{z}{L} < 0 \end{cases}$$

Monin-Obukhov length:

$L = \dfrac{T_{avg}u_*^3}{kHg}$, with a lower limit of -5 and upper limit of +5

Bulk Richardson number:

$Ri = \dfrac{gz(T_{2p} - T_s)}{T_s u^2}$, with a fixed value of 1×10^{-15} if SR>0 and Ri>0

Temperature difference:

$T_d = T_{2p} - T_s$, with an upper limit of -10^{-10} for negative values and a lower limit of 10^{-10} for positive values

Sensible heat flux:

$$H = \begin{cases} \left\{\frac{uT_d}{0.74}\right\}\left\{\frac{k}{\ln(z/z0)}\right\}^2\left\{\frac{1}{(1+4.7Ri)^2}\right\} & \text{Stable, } Ri > 0 \\ \left\{\frac{uT_d}{0.74}\right\}\left\{\frac{k}{\ln(z/z0)}\right\}^2\left\{1-\frac{9.4Ri}{1+5.3[k/\ln(z/z0)]^2\sqrt{|Ri|}}\right\} & \text{Unstable, } Ri < 0 \end{cases}$$

Sub Layer Resistance:

$$R_b = \frac{5}{u_*}\left(\frac{Vi}{Di}\right)^{2/3}$$

Thermal diffusivity:

$$Vi = \frac{145.8\times10^{-4}T_{avg}^{3/2}}{T_{avg}+110.4}$$

Molecular diffusivity:

$$Di = \frac{0.001T_s^{7/4}\sqrt{\frac{1}{MW_{gas}}+\frac{1}{MW_{air}}}}{(D_{air}^{1/3}+D_{gas}^{1/3})^2}$$

where,

$$D_{gas} = 0.369MW_{gas} + 6.29$$
$$D_{air} = 0.369MW_{air} + 6.29$$

Total Surface Resistance:

$$\frac{1}{R_c} = \frac{1-Wst}{R_{st}+R_m} + \frac{1}{R_{ac}+R_g} + \frac{1}{R_{cut}}, \text{ with a lower limit of 10 s/m}$$

Fraction of stomatal blocking under wet conditions:

$$Wst = \begin{cases} 0, & SR \le 200 Wm^{-2} \\ (SR - 200)/800 & 200 < SR \le 600 Wm^{-2} \\ 0.5 & SR > 600 Wm^{-2} \end{cases}$$

Stomatal resistance:

$$R_{st} = \frac{1}{G_s(PAR) f(T) f(D) f(\psi) D_i / D_v}$$

Water diffusivity:

$$D_v = \frac{0.001 T_s^{7/4} \sqrt{\frac{1}{MW_{water}} + \frac{1}{MW_{air}}}}{\left(D_{air}^{1/3} + D_{water}^{1/3}\right)^2}$$

Unstressed leaf stomatal conductance:

$$G_s(PAR) = F_{sun} / r_{st}(PAR_{sun}) + F_{shade} / r_{st}(PAR_{shade})$$

$$F_{sun} = 2\cos\theta\left[1 - e^{-0.5LAI/\cos\theta}\right]$$
$$F_{shade} = LAI - F_{sun}$$

$$r_{st}(PAR) = r_{st\,min}(1 + b_{rs} / PAR)$$

$$PAR_{shade} = \begin{cases} R_{diff} e^{(-0.5LAI^{0.7})} + 0.07 R_{dir}(1.1 - 0.1LAI) e^{-\cos\theta} & LAI < 2.5 \quad or \quad SolarRad < 200 wm^{-2} \\ R_{diff} e^{(-0.5LAI^{0.8})} + 0.07 R_{dir}(1.1 - 0.1LAI) e^{-\cos\theta} & LAI > 2.5 \quad and \quad SolarRad > 200 wm^{-2} \end{cases}$$

$$PAR_{sun} = \begin{cases} R_{do} \cos\alpha / \cos\theta + PAR_{shade} & LAI < 2.5 \quad or \quad SolarRad < 200 wm^{-2} \\ R_{dir}^{0.8} \cos\alpha / \cos\theta + PAR_{shade} & LAI > 2.5 \quad and \quad SolarRad > 200 wm^{-2} \end{cases}$$

Conductance-reducing effects of air temperature T:

$$f(T) = \frac{T - T_{min}}{T_{opt} - T_{min}} \left[\frac{T_{max} - T}{T_{max} - T_{opt}}\right]^{br}$$

where $br = \frac{T_{max} - T_{opt}}{T_{opt} - T_{min}}$

Conductance-reducing effects of water-vapour-pressure deficit D:

$f(D) = 1 - b_{vpd} D$, with a lower limit of 0.1 and a upper limit of 1

Water-vapour-pressure deficit:

$D = E^*(T) - E$

Saturation vapor pressure:

$E^*(T) = 0.6108e^{\frac{17.27(T-273.16)}{T-35.86}}$

Ambient water vapour pressure:

$E = E^*(T)RH$

Conductance-reducing effects of water stress:

$$f(\psi) = \begin{cases} (\psi - \psi_{cs})/(\psi_{c1} - \psi_{c2}) & \psi < \psi_{c1} \\ 1 & \psi \geq \psi_{c1} \end{cases}$$

where $\psi = -0.72 - 0.0013SR$, with a lower limit of 0.1 and upper limit of 1

Mesophyll resistance:

Values of R_m for all dry-depositing species in AURAMS gas-phase chemical mechanism listed in Table 1.

In-canopy aerodynamic resistance:

$$R_{ac} = \frac{R_{ac0} LAI^{1/4}}{u_*^2}$$

where,

R_{ac0}: reference value for in-canopy aerodynamic resistance (Table 1)

LAI: Leaf area index (Table 1)

For some LUCs, a range of R_{ac0} values is given to reflect the change of canopy structure at different times of the growing season. R_{ac0} values for any day of the year based on minimum and maximum LAI values given as:

$$R_{ac0}(t) = R_{ac0}(\min) + \frac{LAI(t) - LAI(\min)}{LAI(Max) - LAI(\min)} \times \left[R_{ac0}(\max) - R_{ac0}(\min)\right]$$

Ground resistance:

$$\frac{1}{R_g(i)} = \frac{\alpha(i)}{R_g(SO_2)} + \frac{\beta(i)}{R_g(O_3)}$$

where,

$$R_g(O_3) = \begin{cases} 2000\ s\ m^{-1} & LUC\ 1-3\ and\ Snow\ Surface \\ 200\ s\ m^{-1} & LUC\ 4-19,\ 25\ and\ 26 \\ 500\ s\ m^{-1} & LUC\ 20-24 \end{cases}$$

For snow surface, $R_g(O_3)$ adjusted by including a snow cover fraction(f_{snow}):

$$\frac{1}{R_g(O_3)} = \frac{1 - 2f_{snow}}{R_g(LUC)} + \frac{2f_{snow}}{R_{snow}}$$

where,

$f_{snow} = \frac{sd}{sd_{\max}}$, note – both f_{snow} and $2f_{snow}$ have a lower limit of 0 and upper limit of 1

$R_{snow} = 2000$ s/m

$$R_g(SO_2) = \begin{cases} 20\ s\ m^{-1} & LUC\ 1\ and\ 3 \\ 70(2-T) & LUC\ 2,\ T\ as\ Surface\ Temperature\ (°C) \\ 50 & LUC\ 4-26,\ Rain \\ 100 & LUC\ 4-26,\ Dew \\ R_{gd},\ (Table\ 1) & LUC\ 4-26,\ Not\ Rain\ or\ Rain,\ T \geq -1°C \\ \min(2R_{gd}, R_{gd}e^{0.2(-1-T)}) & LUC\ 4-26,\ Not\ Rain\ or\ Rain,\ T < -1°C \end{cases}$$

with a lower limit of 100 s/m and upper limit of 500 s/m

For snow surface, $R_g(SO_2)$ are adjusted by snow cover fraction(f_{snow}):

$$\frac{1}{R_g(SO_2)} = \frac{1-2f_{snow}}{R_g(LUC)} + \frac{2f_{snow}}{R_{snow}}$$

where,

$f_{snow} = \frac{sd}{sd_{\max}}$, note – both f_{snow} and $2f_{snow}$ have a lower limit of 0 and upper limit of 1

$R_{snow} = 70(2-T)$, T as °C

Canopy cuticle resistance:

$$R_{cut} = \begin{cases} \frac{R_{cutw0}}{LAI^{1/2}u_*} & Rain\ or\ Dew \\ \frac{R_{cutd0}}{e^{0.03RH}LAI^{1/4}u_*} & Not\ Rain \\ \min(2R_{cut}, R_{cut}e^{0.2(-1-T)}) & T < -1°C \end{cases}$$

where,

$R_{cutw0}(O_3)$ listed in Table 1.
$R_{cutw0}(SO_2)$ = 50 s/m or 100 s/m for rain or dew conditions, respectively.
R_{cutd0} listed in Table 1.

with a lower limit of 100 s/m and 20 s/m for SO_2 dry and wet conditions, respectively

For snow surface, R_{cut} are adjusted by including a snow cover fraction (f_{snow})

$$\frac{1}{R_{cut}} = \frac{1-f_{snow}}{R_{cut}} + \frac{f_{snow}}{R_{snow}}$$

where

$$R_{snow} = \begin{cases} 2000 & O_3 \\ 70(2-T) & SO_2 \end{cases}$$

Roughness length:

$$z_0(t) = z_0(\min) + \frac{LAI(t) - LAI(\min)}{LAI(Max) - LAI(\min)} \times [z_0(\max) - z_0(\min)]$$

Rain or Dew conditions:

$$Condition = \begin{cases} Rain & T > 273.15°K \ \ and \ \ \Pr ec. > 0.1mm/hr \\ Dew & T > 273.15°K \ \ and \ \ u^* . > u^*_{\min} \end{cases}$$

where:

$$u^*_{\min} = \frac{1.5Coedew}{DQ}$$

where:

$$Coedew = \begin{cases} 0.3 & FCLD < 0.25 \\ 0.2 & 0.25 \le FCLD < 0.75 \\ 0.1 & 0.75 \le FCLD \le 1 \end{cases}$$

and

$DQ = 0.0622(1 - RH)E^*(T_s)$, with a lower limit of 0.0001

Parameters (for particulates):

(Variables for computing R_a were not included)

V_d:	deposition velocity (m/s)
R_a:	aerodynamic resistance (s/m)
R_s:	surface resistance (s/m)
u_*:	friction velocity (m/s)
u:	horizontal wind speed at reference height (m/s)
g:	gravitational acceleration (9.81 m/s^2)
T_2:	temperature at reference height (°K)
LAI:	Leaf Area Index
LUC:	Land Use Category (15 LUCs in particle model)
SC:	Season Category (5 SCs in particle model, listed in Table 5)
ρ :	density of particle
dp:	particle diameter
C:	correction factor for small particles
μ :	dynamic viscosity of air
ν :	kinematic viscosity of air
C:	Cunningham slip correction factor
E_B:	collection efficiency from Brownian diffusion
E_{IM}:	collection efficiency from impaction
E_{IN}:	collection efficiency from interception
R1:	correction factor representing fraction of particles that sticks to surface
Sc:	Schmidt number
D:	Brownian diffusivity
St:	Stokes number
K:	Boltzmann constant (gm cm^2/s^2-°K)
P:	surface pressure (kPa)
λ :	mean free path of air molecules

Deposition Velocity:

$$V_d = V_g + \frac{1}{R_a + R_s}$$

Assumes SO_4^{2-} and NH_4^+ have the same V_d; and NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, and K^+ have the same V_d as described in Cheng et al. (2001).

Mass median diameter (MMD) and geometric standard deviation (GSD) for SO_4^{2-} chosen as 0.35 µm and 2.0 µm, respectively as reported in Wesely et al. (1985).

MMD and GSD for Na^+ are taken as 5.12 µm and 2.64 µm, respectively as reported in Ruijgrok et al (1997).

Gravitational settling velocity:

$$V_g = \frac{\rho d_p^2 g C}{18\mu}$$

Cunningham slip correction factor:

$$C = 1 + \frac{2\lambda}{d_p}(1.257 + 0.4e^{-0.55 d_p/\lambda})$$

Aerodynamic Resistance:

R_a is computed with the same approach as the gas model, but the parameters are adapted from Table 4.

Surface Resistance:

$$R_s = \frac{1}{\varepsilon_0 u_* (E_B + E_{IM} + E_{IN}) R_1}, \text{ with a lower limit of 5}$$

where ε_0 is an empirical constant chosen as 3 for all LUCs

Collection efficiency from Brownian diffusion:

$$E_B = Sc^{-\gamma}$$

where γ lies between $^1/_2$ and $^2/_3$ with larger values for rougher surfaces. (Table 4)

Schmidt number:

$$Sc = \nu / D$$

Collection efficiency from impaction:

$$E_{IM} = \left(\frac{St}{\alpha + St} \right)^{\beta}$$

where,

a: constant varying with LUC (Table 4)
b: constant, chosen as 2

Stokes number:

$$St = \begin{cases} \dfrac{V_g u_*^2}{\nu} & \textit{smooth surface, LUC8, 9, 12, 13, and 14} \\ \dfrac{V_g u_* A}{g} & \textit{vegetated surface, LUCs other than above} \end{cases}$$

where A is the characteristic radius varying with LUC and season (Table 4)

Collection efficiency from interception:

$E_{IN} = \frac{1}{2}\left(\frac{d_p}{A} \right)^2$, with a upper limit of 0.6

where A is the characteristic radius varying with LUC and season (Table 4)

Correction factor representing fraction of particles that sticks to the surface:

$R_1 = \exp(-St^{1/2})$, with a low limit of 0.5

Mean free path of air molecules:

$$\lambda = 6.54 \times 10^{-8} \frac{\mu}{1.818 \times 10^{-5}} \frac{101.3}{P} \left(\frac{T_2}{293.15} \right)^{1/2}$$

Brownian diffusivity:

$$D = \frac{CKT_2}{3\pi d_p \mu}$$

Dynamic viscosity of air:

$$\mu = \frac{145.8 \times 10^{-8} T_2^{3/2}}{T_2 + 110.4}$$

Kinematic viscosity of air:

$$\nu = \frac{\mu}{\rho_{air}}$$

Table 1. LUC and all related parameters (all resistance have units of s/m; na = not applicable; f(u) = function of wind speed).

	LUC	R_{lu}	$R_{lu,ac}$ O_3	$R_{lu,ac}$ O_3	$R_{lu,ac}$ SO_2	R_{gs} SO_2	$r_{s,min}$ (s/m)	b_{rs} (Wm^{-2})	T_{min} (°C)	T_{max} (°C)	T_{lat} (°C)	b_{VPD} (kPa^{-1})	$\Psi_{1,1}$ (Mpa)	$\Psi_{1,2}$ (Mpa)	z_0 (m)	Sd_{max} (cm)
1	water	0	na	na	na	20	na	na	na	na	na	na	na	na	f(u)	na
2	ice	0	na	na	na	Eq. (8a)	na	na	na	na	na	na	na	na	0.01	1
3	inland lake	0	na	na	na	20	na	na	na	na	na	na	na	na	f(u)	na
4	evergreen needleleaf trees	100	4000	200	2000	200	250	44	−5	40	15	0.31	−2	−2.5	0.9	200
5	evergreen broadleaf trees	250	6000	400	2500	100	150	40	0	45	30	0.27	−1	−5.0	2.0	400
6	deciduous needleleaf trees	60–100	4000	200	2000	200	250	44	−5	40	15	0.31	−2	−2.5	0.4–0.9	200
7	deciduous broadleaf trees	100–250	6000	400	2500	200	150	43	0	45	27	0.36	−1.9	−2.5	0.4–1.0	200
8	tropical broadleaf trees	300	6000	400	2500	100	150	40	0	45	30	0.27	−1	−5.0	2.5	400
9	drought deciduous trees	100	8000	400	6000	300	250	44	0	45	25	0.31	−1	−4.0	0.6	200
10	evergreen broadleaf shrubs	60	6000	400	2000	200	150	40	0	45	30	0.27	−2	−4.0	0.2	50
11	deciduous shrubs	20–60	5000	300	2000	200	150	44	−5	40	15	0.27	−2	−4.0	0.05–0.2	50
12	thorn shrubs	40	5000	300	2000	200	250	44	0	45	25	0.27	−2	−3.5	0.2	50
13	short grass and forbs	20	4000	200	1000	200	150	50	5	40	30	0	−1.5	−2.5	0.04	5
14	long grass	10–40	4000	200	1000	200	100	20	5	45	25	0	−1.5	−2.5	0.02–0.1	20
15	crops	10–40	4000	200	1500	200	120	40	5	45	27	0	−1.5	−2.5	0.02–0.1	10
16	rice	10–40	4000	200	1500	50	120	40	5	45	27	0	−1.5	−2.5	0.02–0.1	10
17	sugar	10–40	4000	200	2000	200	120	50	5	45	25	0	−1.5	−2.5	0.02–0.1	10
18	maize	10–50	5000	300	2000	200	250	65	5	45	25	0	−1.5	−2.5	0.02–0.1	10
19	cotton	10–40	5000	300	2000	200	125	65	10	45	30	0	−1.5	−2.5	0.02–0.2	10
20	irrigated crops	20	4000	200	2000	50	150	40	5	45	25	0	−1.5	−2.5	0.05	10
21	urban	40	6000	400	4000	300	200	42	0	45	22	0.31	−1.5	−3	1.0	50
22	tundra	0	8000	400	2000	300	150	25	−5	40	20	0.24	0	−1.5	0.03	2
23	swamp	20	5000	300	1500	50	150	40	0	45	20	0.27	−1.5	−2.5	0.1	10
24	Desert	0	na	na	na	700	na	na	na	na	na	na	na	na	0.04	2
25	mixed wood forests	100	4000	200	2500	200	150	44	−3	42	21	0.34	−2	−2.5	0.6–0.9	200
26	Transitional forest	100	4000	200	2500	200	150	43	0	45	25	0.31	−2	−3	0.6–0.9	200

Table 2. LAI(i) values dependent upon Land Use Category (LUC) ("i" represents month number, "i=14" and "i=15" represent minimum and maximum value, respectively).

No.	LUC	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	water	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	ice	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3	inland lake	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	evergreen needleleaf trees	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
5	evergreen broadleaf trees	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
6	deciduous needleleaf trees	0.1	0.1	0.5	1.0	2.0	4.0	5.0	5.0	4.0	2.0	1.0	0.1	0.1	0.1	5.0
7	deciduous broadleaf trees	0.1	0.1	0.5	1.0	2.0	4.0	5.0	5.0	4.0	2.0	1.0	0.1	0.1	0.1	5.0
8	tropical broadleaf trees	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
9	drought deciduous trees	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
10	evergreen broadleaf shrubs	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
11	deciduous shrubs	0.5	0.5	1.0	1.0	1.5	2.0	3.0	3.0	2.0	1.5	1.0	0.5	0.5	0.5	3.0
12	thorn shrubs	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
13	short grass and forbs	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
14	long grass	0.5	0.5	0.5	0.5	0.5	0.5	1.0	2.0	2.0	1.5	1.0	1.0	0.5	0.5	2.0
15	crops	0.1	0.1	0.1	0.5	1.0	2.0	3.0	3.5	4.0	0.1	0.1	0.1	0.1	0.1	4.0
16	rice	0.1	0.1	0.1	0.5	1.0	2.5	4.0	5.0	6.0	0.1	0.1	0.1	0.1	0.1	6.0
17	sugar	0.1	0.1	0.1	0.5	1.0	3.0	4.0	4.5	5.0	0.1	0.1	0.1	0.1	0.1	5.0
18	maize	0.1	0.1	0.1	0.5	1.0	2.0	3.0	3.5	4.0	0.1	0.1	0.1	0.1	0.1	4.0
19	cotton	0.1	0.1	0.1	0.5	1.0	3.0	4.0	4.5	5.0	0.1	0.1	0.1	0.1	0.1	5.0
20	irrigated crops	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
21	urban	0.1	0.1	0.1	0.1	0.5	1.0	1.0	1.0	1.0	1.0	0.4	0.1	0.1	0.1	1.0
22	tundra	1.0	1.0	0.5	0.1	0.1	0.1	0.1	1.0	2.0	1.5	1.5	1.0	1.0	0.1	2.0
23	swamp	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
24	Desert	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
25	mixed wood forests	3.0	3.0	3.0	4.0	4.5	5.0	5.0	5.0	4.0	3.0	3.0	3.0	3.0	3.0	5.0
26	Transitional forest	3.0	3.0	3.0	4.0	4.5	5.0	5.0	5.0	4.0	3.0	3.0	3.0	3.0	3.0	5.0

Table 3. Species-specific chemical and physical parameters.[a]

No.	Symbol	Name	Depn Mmts	MW	H (M atm^{-1})	H* (M atm^{-1})	pe^{b} (W)	Rm	a	b
1	SO_2	Sulphur dioxide	Yes	64	(1.1-1.5) x 10^{0}	2.65 x 10^{5}	75.5 to -7.6	0	1	0
2	H_2SO_4	Sulphuric acid	No	98	2.1 x 10^{5}	>2.1 x 10^{5}	4.9 to -4.3	0	1	1
F	NO	Nitric oxide	Yes	30	(1.4-1.9) x10^{-3}	H	27.8 to 3.0	Not considered		
3	NO_2	Nitrogen dioxide	Yes	46	(0.7-4.1) x 10^{-2}	H	28.4 to 8.2	0	0	0.8
4	O_3	Ozone	Yes	48	(0.9-1.3) x 10^{-2}	H	28.1 to 18.6	0	0	1
5	H_2O_2	Hydrogen peroxide	Yes	34	(0.7-1.4) x 10^{5}	H	24.8 to 9.7	0	1	1
6	HNO_3	Nitric acid	Yes	63	(0.1-2.6) x 10^{6}	3.2 x 1013	14.1 to 8.9	0	10	10
7	HONO	Nitrous acid	Yes	47	(3.7-5.0) x 10^{1}	2.6 x 105	17.5 to 14.8	0	2	2
8	HNO_4	Pernitric acid	No	79	(0.1-1) x 10^{5}	>1 x 107	No data	0	5	5
9	NH_3	Ammonia	Yes	17	(1.0-7.8) x 10^{1}	1.1 x 104	Not applicable	0	1	0
10	PAN	Peroxyacetylnitrate	Yes	121	(2.8-5.0) x 10^{0}	H	30.2 to -1.5	0	0	0.6
11	PPN	Peroxypropylnitrate	No	135	2.9 x 10^{0}	H	37.8 to -2.3	0	0	0.6
12	APAN	Aromatic acylnitrate	No	183	No data	5	46.9 to 11.2	0	0	0.8
13	MPAN	Peroxymethacrylic nitric anhydride	No	147	1.7 x 10^{0}	H	3.1	0	0	0.3
14	HCHO	Formaldehyde	Yes	30	(0.3-1.4) x 10^{4}	4.9 x 103	3.0 to -0.1	0	0.8	0.2
15	MCHO	Acetaldehyde	No	44	(1.0-1.7) x 10^{1}	≥15	-1.0 to -3.9	100	0	0.05
16	PALD	C3 carbonyls	No	58	(2.4-3.7) x 10^{0}	H	-1.3 to -1.8	100	0	0.05
17	C4A	C4–C5 carbonyls	No	72	(0.9-1.8) x 10^{1}	H	-1.3 to -1.8	100	0	0.05
18	C7A	C6–C8 carbonyls	No	128	(0.4-11) x 10^{1}	H	-1.5	100	0	0.05
19	ACHO	Aromatic carbonyls	No	106	(3.5-4.2) x 10^{1}	H	-1.0 to -2.5	100	0	0.05
20	MVK	Methyl-vinyl-ketone	No	70	(2.1-4.4) x 10^{1}	H	0.2	0	0	0.05
21	MACR	Methacrolein	No	70	(4.3-6.5) x 10^{0}	H	-1.2	100	0	0.05
22	MGLY	Methylglioxal	No	72	(0.4-3.2) x 10^{4}	H	-0.7	0	0.01	0
23	MOH	Methyl alcohol	No	32	(1.4-2.3) x 10^{2}	≥H	3.0	0	0.6	0.1
24	ETOH	Ethyl alcohol	No	46	(1.2-2.3) x 10^{2}	≥H	-1.3 to -2.9	0	0.6	0
25	POH	C3 alcohol	No	60	(0.9-1.7) x 10^{2}	≥H	-0.3	0	0.4	0
26	CRES	Cresol	No	104	8.3 x 10^{2}	H	-2.5	0	0.01	0
27	FORM	Formic acid	Yes	46	(0.9-8.9) x 10^{3}	9.8 x 10^{6}	1.9 to -6.4	0	2	0
28	ACAC	Acetic acid	Yes	60	(0.8-9.3) x 10^{3}	9.6 x 10^{5}	-3.1 to -9.6	0	1.5	0
29	ROOH	Organic peroxides	Yes	48	(0.1-3.1) x 10^{2}	H	4.2 to 3.6	0	0.1	0.8
30	ONIT	Organic nitrates	No	77	2.0 x 10^{0}	H	10.5 to -5.0	100	0	0.5
31	INIT	Isoprene nitrate	No	147	2.0 x 10^{0}	H	No data	100	0	0.5

[a] Values for Henry's Law constant (H) were obtained from Howard and Meylan (1997) and Sander (1999).

Table 4. Parameters related to LUC and SC in particle model.

NO.	Land use categories Description (LUC)	Z_0 (m)					A (mm)						
		SC 1	SC 2	SC 3	SC4	SC 5	SC 1	SC 2	SC 3	SC 4	SC 5		
1	Evergreen)needleleaf trees	0.8	0.9	0.9	0.9	0.8	2	2	2	2	2	1	0.56
2	Evergreen broadleaf trees	2.65	2.65	2.65	2.65	2.65	5	5	5	5	5	0.6	0.58
3	Deciduous needleleaf trees	0.85	0.85	0.8	0.55	0.6	2	2	5	5	2	1.1	0.56
4	Deciduous broadleaf trees	1.05	1.05	0.95	0.55	0.75	5	5	10	10	5	0.8	0.56
5	Mixed broadleleaf and needleaf trees	1.15	1.15	1.15	1.15	1.15	5	5	5	5	5	0.8	0.56
6	Grass	0.1	0.1	0.05	0.02	0.05	2	2	5	5	2	1.2	0.54
7	Crops, mixed farming	0.1	0.1	0.02	0.02	0.05	2	2	5	5	2	1.2	0.54
8	Desert	0.04	0.04	0.04	0.04	0.04	na	na	na	na	na	50	0.54
9	Tundra	0.03	0.03	0.03	0.03	0.03	na	na	na	na	na	50	0.54
10	Shrubs and interrupted wood-lands	0.1	0.1	0.1	0.1	0.1	10	10	10	10	10	1.3	0.54
11	Wet land with plants	0.03	0.03	0.02	0.02	0.03	10	10	10	10	10	2	0.54
12	Ice cap and glacier	0.01	0.01	0.01	0.01	0.01	na	na	na	na	na	50	0.54
13	Inland water	f (u)	f (u)	f(u)	f(u)	f (u)	na	na	na	na	na	100	0.5
14	Ocean	f (u)	f (u)	f(u)	f(u)	f (u)	na	na	na	na	na	100	0.5
15	Urban	1	1	1	1	1	10	10	10	10	10	1.5	0.56

Table 5. Latitude values applied for the determination of Seasonal categories (SC) used in particle model.

NO.	Seasonal categories (SC)	Month											
		12	1	2	3	4	5	6	7	8	9	10	11
1	Midsummer with lush vegetation.	<30			<35			<55	<70	<45	<35		
2	Autumn with cropland that has not been harvested.									45-80	35-65	35-45	35-40
3	Late autumn after frost, no snow.										65-80	45-65	40-50
4	Winter, snow on ground and sub-freezing.				>40	>45	>60	>70	>80			>65	>50
5	Transitional spring with partially green short annuals.	30-35			35-40	35-45	35-60	55-70	70-80				

APPENDIX III

WBEA Dry Deposition Calculation Methods for Gases (SO_2 and NO_2)

(after EPCM, 2002, 2000)

Parameters:

V_d: deposition velocity (m/s)
R_a: aerodynamic resistance (s/m)
R_b: boundary-layer resistance (s/m)
R_c: surface resistance (s/m)
θ: standard deviation of wind direction (rad)
u_*: friction velocity (m/s)
u: horizontal wind speed at reference height (m/s)
SR: solar radiation (w/m^2)
SW: surface wetness

Deposition Velocity:

$$\mathbf{V_d} = \frac{1}{(R_a + R_b + R_c)}$$

Aerodynamic Resistance:

$$R_a = \begin{cases} \dfrac{4}{u\theta^2} & \textit{Stable conditions, night time } (SR \le 5w/m^2) \textit{ or } \theta < 0.2rad \\ \dfrac{9}{u\theta^2} & \textit{Unstable conditions, day time } (SR > 5w/m^2) \textit{ and } \theta > 0.2rad \end{cases}$$

– with an upper limit of 1000
– u has a lower limit of 0.36m/s

Boundary-Layer Resistance for SO_2:

$$R_b = \frac{7.225}{u^*}$$

– with an upper limit of 1000, where $u^* = \left(\dfrac{u}{R_a}\right)^{0.5}$

Boundary-Layer Resistance for NO_2:

$$R_b = \frac{6.18}{u^*}$$

Surface Resistance:

Same as Alberta Environment method (Appendix I), where dry/wet conditions determined by SW:

SW >0.1, wet conditions
SW ≤0.1, dry conditions